

Process for obtaining methionine

The invention provides a method for isolating D,L-methionine with bulk densities > 550 g/l from solutions containing D,L-methionine ammonium salt.

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Prior art

Methods for producing D,L-methionine are known in which the D,L-methionine is initially obtained as ammonium methioninate.

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According to US20050176115, an aqueous, ammonium-containing D,L-methionine solution is obtained by reacting aqueous solutions of 2-amino-4-methylthiobutyronitrile already in the presence of NH_3 using biocatalysts to give D,L-methionine. The D,L-methionine is then precipitated by removing the ammonia under reduced pressure. The D,L-methionine thus obtained has a purity of 99%. The bulk density of the D,L-methionine obtained is not stated.

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Likewise in JP2004-254690, D,L-methionine and NH_3 are formed by reacting 2-amino-4-methylthiobutyronitrile with a biocatalyst. The solubility of the methionine is increased by the presence of ammonia which facilitates the removal of the biocatalyst. The exact isolation conditions and the product properties of the D,L-methionine are not stated in JP2004-254690.

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DE 60127538 describes a method in which D,L-methionine is produced from methionine amide by a catalyzed saponification reaction. Here the ammonia is completely removed from the resulting ammonium methioninate solution by stripping and the methionine is crystallised out, although the bulk densities of the methionine obtained are not stated.

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In WO 2008006977, D,L-methionine is obtained from methionine hydantoin by saponification with NH_3 and the D,L-methionine is obtained by evaporation of NH_3 and CO_2 under reduced pressure. Nothing is stated concerning the product properties.

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WO2007034065 also describes an ammoniacal saponification of methionine hydantoin. The ammonia is removed from the ammonium methioninate solution in a stripping column and the methionine is subsequently precipitated by cooling the solution. The product properties of the methionine formed are not mentioned therein.

5 DE 10238212 describes a method in which methionine hydantoin is saponified in water at high temperatures with or without catalyst. NH_3 and CO_2 are partially removed before crystallization of the resulting methionine. No mention is made of the residual amounts of CO_2 and ammonia in the solution from which the crystallization takes place, nor is anything revealed concerning the bulk density of the resulting
10 methionine.

WO 2003050071 describes aqueous mixtures of fatty acid polyethylene glycol esters with modified celluloses, which are used as auxiliaries in the crystallization of methionine from potassium methioninate solutions neutralized with carbon dioxide from the alkaline saponification of methionine hydantoin. In these particular methods
15 in the presence of large amounts of potassium, bulk densities of up to 586g/l are obtained, in one case of 620g/l (with hydroxyethylcellulose additive). No details are given, however, for crystallization of D,L-methionine from solutions containing D,L-ammonium methioninate.

20 The solubility of D,L-methionine is increased in the presence of NH_3 (see solubility curves from JP2004-254690).

For an economic method for isolating D,L-methionine, it is accordingly advantageous to remove the ammonia as completely as possible in order to maximize the amount of crystallizable D,L-methionine. For this purpose, the ammonia may be removed by
25 various methods known from the literature, such as stripping, evaporation under reduced pressure etc.

30 **Object of the invention**

The object of the invention is to provide a method for isolating D,L-methionine, starting from solutions containing ammonium methioninate, in which the D,L-methionine is obtained with high bulk densities of > 550 g/l.

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Description

The present investigations have shown that the D,L-methionine when crystallized from aqueous solutions is typically obtained with low bulk densities of < 550 g/l. A
10 significant increase in the bulk density could not be achieved solely by the addition of crystallization additives. Surprisingly, it has been shown that a residual amount of NH_3 in combination with added additives results in D,L-methionine with higher bulk density.

Since in aqueous solutions comprising both NH_3 and methionine an equilibrium is
15 established between ammonium methioninate on one side and methionine and ammonia on the other side, reference is made only to the NH_4^+ concentrations below for simplicity, irrespective of whether this relates to NH_4^+ or NH_3 .

The object mentioned above and also other related but not explicitly stated objects
20 are achieved by the provision of a method for crystallizing D,L-methionine from aqueous solutions and/or suspensions containing D,L-methionine and D,L-methionine ammonium salt, having a Met content (comprising the total methionine in the form of D,L-methionine and D,L-methionine ammonium salt) of $70 - 180$ g/kg of solution and/or suspension ($7 - 18\%$ by weight),
25 preferably $90 - 150$ g/kg ($9 - 15\%$ by weight), an NH_4^+ content of $1 - 5$ g/kg of solution and/or suspension ($0.1 - 0.5\%$ by weight), preferably 1.5 to 3.0 g/kg ($0.15 - 0.3\%$ by weight), in the presence of a crystallization additive,
which comprises a nonionic or anionic surfactant or a mixture of various nonionic or
30 anionic surfactants,

in which the temperature of the solution and/or suspension is lowered directly or stepwise from a temperature range of $T_1 = 85 - 110^\circ\text{C}$ to a temperature range of $T_2 = 30 - 50^\circ\text{C}$, so that methionine precipitates as a solid from the solution and/or suspension.

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Aqueous solution containing D,L-methionine and D,L-methionine ammonium salt is understood to mean here that the predominant proportion of the total methionine (Met) present is dissolved and only low Met proportions of max. 5% are present undissolved, i.e. suspended.

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Aqueous suspension containing D,L-methionine and D,L-methionine ammonium salt is understood to mean here that a significant proportion, namely of $> 5\%$, of the total methionine present is suspended, while the remainder is present in dissolved form.

15 Correspondingly, the optimal NH_4^+ concentration, based on methionine, is at least ca. $5 \text{ g NH}_4^+ / \text{kg Met}$ and not more than ca. $60 \text{ g NH}_4^+ / \text{kg Met}$, when the methionine concentration in the solution is in the range of 90 g/kg to 150 g/kg .

20 The NH_4^+ concentration may in this case be determined, for example, using an NH_4^+ -sensitive electrode according to known methods. The NH_4^+ concentration is generally determined in this case by measurement on a sample solution adjusted to pH 11 and comparing with the measurement on NH_4Cl solutions of known concentration also adjusted to pH 11.

25 The methionine concentration in the solution and/or suspension is most easily determined by HPLC.

30 By means of the combination described of the presence of NH_4^+ ions, the addition of crystallization additive and the temperature regulation of the crystallization and using the method according to the invention, coarse-grained methionine crystals which may be readily filtered and having a bulk density of $> 550 \text{ g/l}$ after drying are obtained.

Suitable as anionic surfactants are particularly surfactants according to one of the compounds depicted in formulae 1 to 3, or mixtures thereof:



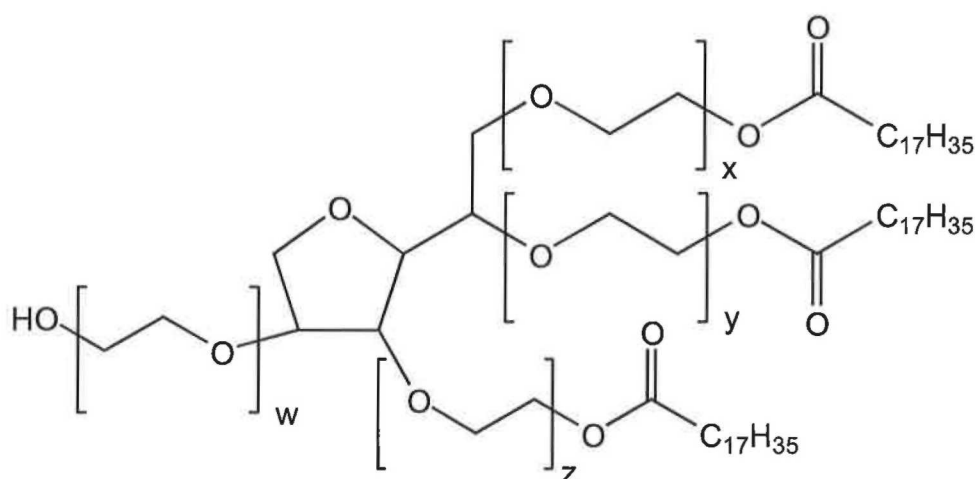
where n is an integer from 1 to 10, M is sodium or potassium and R^1 , R^2 and R^3 are a linear, branched or cyclic, saturated or unsaturated C_8 - to C_{20} -alkyl group or an aryl group. Relatively high bulk densities of 564 to 588 kg/l were obtained with these

10 surfactants, as shown in Table 1 in Example 1 with the additives 2, 3 and 4.

Preference is given to using surfactants in which n equals 2 and R^1 , R^2 and R^3 are linear, saturated C_8 - to C_{18} -alkyl groups, since these are readily commercially available and effective.

- 15 Particular preference is given to using anionic surfactants of the formulae
 $C_nH_{2n+1}-O-SO_3Na$, where n = 12 to 18 (Sulfopon® 1218G, Oleochemicals)
 $C_nH_{2n+1}-O-C_2H_4-SO_3Na$, where n = 8 to 18 (Hostapon® SCI 85, Clariant)
 $C_nH_{2n+1}-(OC_2H_4)_2-O-SO_3Na$, where n = 12 (Disponil® FES 27, Cognis)

- 20 In a preferred embodiment of the method, the nonionic surfactant used is a sorbitan fatty acid ester or a mixture of various sorbitan fatty acid esters, particularly preferably polyethoxylated sorbitan fatty acid esters. Sorbitan fatty acid esters have the advantage that they are effective and readily commercially available. In a very particularly preferred embodiment, the nonionic surfactant is a polyethoxylated
25 sorbitan tristearate according to formula 4:



(formula 4)

where $w+x+y+z=20$.

With these surfactants, a relatively high bulk density of 578 kg/l was obtained, as shown in Example 3.

The concentration of the crystallization additive (based on the active ingredient) in the solution and/or suspension from which the crystallization takes place is preferably at least 700 ppm and not more than 4000 ppm, based on the total mass of the solution and/or suspension, particularly preferably at least 750 ppm and not more than 2000 ppm, most particularly preferably at least 800 ppm and not more than 1000 ppm. This ensures a good development of the additive effect without introducing too many foreign materials into the product solution.

In order to achieve an optimal dosage and distribution of the crystallization additive, the latter is preferably used in the form of an aqueous solution or emulsion, wherein the concentration of the crystallization additive in the solution or emulsion is preferably 2 to 15% by weight.

In a preferred embodiment of the method according to the invention, the solution from which the crystallization takes place additionally comprises a defoamer. The function of the defoamer is to suppress the foam occurring during the handling of the methionine solution and/or suspension and caused or intensified by some of the crystallization additives mentioned above. Moreover, a synergistic effect arises, surprisingly, during simultaneous use of defoamer and crystallization additives in the

case of the bulk densities of the methionine achieved, whereby bulk densities of even over 600 g/l are attained and simultaneously the negative effects of enrichment processes are avoided and therefore the method according to the invention can also be carried out in continuous mode. This is particularly apparent by comparing
5 experiments 2, 3 and 4 (without added defoamer -> bulk densities of 564-588 kg/l)) with experiments 8, 9 and 10 (with added defoamer -> bulk densities of 630-634 kg/l) respectively in Table 1 of Example 1. In addition, this embodiment enables the use of less crystallization additive.

- 10 Preference is given to using defoamers comprising silicone oil, since these have proven to be particularly effective, wherein preferably a silicone oil having a kinematic viscosity of 0.65 to 10 000 mm²/s (measured at 25°C according to DIN 53018), particularly preferably 90 to 1500 mm²/s, is used. The defoamer may furthermore comprise constituents which are effective as emulsifiers, for example
15 mixtures of polyethoxylated fatty acids and polyethoxylated fatty alcohols. The defoamer may likewise comprise silica. In a preferred embodiment, the defoamer is an aqueous solution comprising 5 to 10% by weight silicone oil, 0.05 to 1% by weight silica, 0.5 to 5% by weight of a mixture of polyethoxylated fatty acids, and 2 to 7% by weight of a mixture of polyethoxylated fatty alcohols.
- 20 Preference is given to using the defoamer in a mixture with the crystallization additive. In order to achieve a continuous, stable dosage of the defoamer, it is preferably further diluted with water prior to use.

- The use of silicone oil defoamers means that silicon may be detected in the
25 methionine produced by the method according to the invention using a suitable analytical method (e.g. X-ray photoelectron spectroscopy, abbreviated to XPS).

- Preference is given to using the defoamer in the method according to the invention such that the weight ratio of the defoamer: crystallization additive (based on the
30 active ingredient) in the solution or suspension from which the crystallization takes place, is in the range of 4:1 to 1:1, preferably in the range of 3:1 to 2:1 and the

concentration of the crystallization additive (based on the active ingredient) is in this case at least 50 ppm and not more than 1200 ppm, based on the total mass of the solution and/or suspension, preferably 100 ppm to 600 ppm, particularly preferably 200 ppm to 400 ppm. The high D,L-methionine bulk densities achieved in this case of
5 significantly above 600 g/l can be particularly effectively seen in Example 4/Table 3.

The method according to the invention is in this case preferably carried out such that the crystallization takes place by introducing an aqueous solution and/or suspension containing D,L-methionine and D,L-methionine ammonium salt heated to 85 to 110°C
10 into an aqueous solution and/or suspension containing D,L-methionine and D,L-methionine ammonium salt warmed to 30 to 50°C, wherein the temperature of the resulting mixture is constantly maintained between 30 and 50°C.

Very particular preference is given in this case to introducing an aqueous solution
15 containing D,L-methionine and D,L-methionine ammonium salt heated to 85 to 110°C into an aqueous suspension containing D,L-methionine and D,L-methionine ammonium salt warmed to 30 to 50°C. This has the advantage that crystals are obtained which may be particularly effectively filtered.

A further preferred embodiment of the method is characterized in that the
20 crystallization is carried out in two stages, wherein, in the first crystallization stage, a solution and/or suspension containing D,L-methionine and D,L-methionine ammonium salt heated to 85 to 110°C is introduced into a suspension containing D,L-methionine and D,L-methionine ammonium salt warmed to 60 to 80°C and the
25 temperature of the resulting mixture is constantly maintained between 60 and 80°C and wherein the suspension containing D,L-methionine and D,L-methionine ammonium salt warmed to 60 to 80°C obtained in the first crystallization stage is introduced in a second crystallization stage into a suspension containing D,L-methionine and D,L-methionine ammonium salt warmed to 30 to 50°C, wherein the
30 temperature of the resulting mixture is constantly maintained between 30 and 50°C. In this case the proportion of impurities in the crystallization broth can be particularly

effectively controlled or can be depleted by discharging at a suitable point, without relinquishing the advantageous effect of the bulk density above 550 g/l.

A furthermore preferred embodiment of the method according to the invention is characterized in that the crystallization is carried out by vacuum crystallization, wherein the pressure in the first crystallization stage is 60 to 1000 mbar and, if a two-stage crystallization is carried out, the pressure in the second crystallization stage is 35 to 200 mbar. This has the advantage that surfaces employed are less cold. Cold surfaces may lead to undesired local caking.

The aqueous solutions and/or suspensions containing D,L-methionine and D,L-methionine ammonium salts used for the crystallization method according to the invention may be prepared beforehand by dissolving and/or suspending D,L-methionine in water in the presence of appropriate amounts of ammonia. The methionine may originate from any manufacturing process which renders the method universally applicable.

It has proven to be advantageous in this case that D,L-methionine having a methionine content of at least 90% by weight, preferably at least 95% by weight, is used for the dissolution.

Particularly suitable for this purpose is D,L-methionine in the form of pure methionine and/or crude methionine from any manufacturing process having a residual moisture of 0.1 to 9.5% by weight, preferably 0.2 to 4.5% by weight. The use of pure or crude methionine of a quality which is still filter-moist from an industrial process for preparing D,L-methionine is advantageous, since in this manner D,L-methionine with the desired properties, particularly the bulk density > 550 kg/l, may be obtained directly at the end of the process after drying.

The method according to the invention is also particularly suitable for isolating D,L-methionine from aqueous solutions and/or suspensions containing D,L-methionine

and D,L-methionine ammonium salts which have been prepared by hydrolysis of D,L-methionine nitrile and/or D,L-methionine amide, specifically without the use of salt-forming acidic or basic saponification agents (such as HCl, H₂SO₄ or alkali metal hydroxides such as NaOH or KOH) other than ammonia. Such non-salt-forming
5 saponification agents or saponification catalysts such as TiO₂ or MnO₂ are known from the relevant patent literature and, like ammonia as saponification agent in the saponification of D,L-methionine nitrile and/or D,L-methionine amide, directly yield aqueous solutions and/or suspensions containing D,L-methionine and D,L-methionine ammonium salts from which D,L-methionine may be obtained by
10 crystallization by the method according to the invention. Such aqueous solutions and/or suspensions therefore contain practically no alkali metal ions, such as Na⁺ or K⁺ ions.

Accordingly, a further subject of the invention is a
15 method for preparing D,L-methionine, in which an aqueous solution of D,L-methionine ammonium salt is initially formed by hydrolysis of D,L-methionine nitrile and/or D,L-methionine amide, and an aqueous solution and/or suspension containing D,L-methionine and D,L-methionine ammonium salt is produced therefrom by partial removal of the ammonia from the D,L-methionine ammonium salt, which is present
20 therein bound as ammonium ion, from which D,L-methionine is then obtained by the crystallization method according to the invention.

In the method according to the invention, the ammonium methioninate solution primarily formed is therefore initially subjected to ammonia depletion. Methods for this
25 purpose are known: this may be achieved, for example, by heating under reduced pressure or by stripping with steam.

Accordingly, the method according to the invention for preparing D,L-methionine is preferably carried out such that the aqueous solution of D,L-methionine ammonium
30 salt is brought to an NH₄⁺ content of 1 – 5 g/kg of the solution and/or suspension,

preferably 1.5 to 3.0 g/kg, by evaporating and/or stripping off of ammonia prior to the crystallization, e.g. by heating under reduced pressure or by stripping with steam.

Here, the ammonium concentration in accordance with the invention is only depleted,
5 however, to values in a range of ca. 5 to ca. 60 g NH_3 /kg of methionine. In this case, it is advantageous to select a temperature sufficiently high such that D,L-methionine does not already precipitate during the removal of ammonia but remains in solution. The hot methionine solution is preferably rapidly cooled down by feeding into a precharged, cooler methionine suspension, whereby an overconcentration of
10 dissolved D,L-methionine is generated and D,L-methionine precipitates from the solution.

A procedure may also be employed here in which the aqueous solution and/or suspension of D,L-methionine and/or D,L-methionine ammonium salt is brought to
15 the appropriate Met content of 70 – 180 g/kg of the solution, preferably 90 to 150 g/kg of the solution, by addition of water and/or D,L-methionine, which renders the method of variable and flexible use.

The precipitated D,L-methionine is preferably separated from the resulting mother
20 liquor and dried or is initially recrystallized and is dried after separation from the mother liquor obtained in this case, whereupon D,L-methionine with a purity of at least 99% by weight and a bulk density of at least 550 g/l after drying is finally obtained.

25 The mother liquor obtained here is preferably fed back into a crystallization stage, which results in minimization of losses of methionine.

The method may either be carried out continuously or batchwise.

30 Fig. 1 shows by way of example and schematically the continuous procedure of the method according to the invention. The ammonium methioninate solution is initially

fed into a suitable apparatus A for reduction of the ammonia concentration. This is generally an evaporation system, e.g. comprising a falling-film evaporator or circulation evaporator. The conditions here are selected such that an NH_3 amount of 1 to 5 g/kg of the solution and/or suspension is present in the product stream, while
5 the Met concentration is in a range of 70 – 180 g/kg of the solution and/or suspension, preferably 90 - 150 g/kg. The crystallization additive according to the invention, optionally including defoamer, is added continuously to this product stream. The temperature of the solution and/or suspension containing D,L-methionine and/or D,L-methionine ammonium salt is preferably 90 to 100°C. This
10 Met solution and/or suspension may be heated to 100 to 110°C if required by means of one or more heat exchangers B and subsequently may be preferably rapidly cooled in one or more stages to temperatures between 30 and 50°C in a suitable crystallization apparatus C, whereupon the D,L-methionine crystallizes out. If required, the D,L-methionine suspension may be fed into an intermediate vessel D in
15 order to allow a postprecipitation of D,L-methionine. Finally, the D,L-methionine is isolated in a suitable solid/liquid separation step E, such as a filtration or centrifugation, whereupon the filtrate obtained can be fed back, if required, into the feed to apparatus A. This can lead to an enrichment of the additives according to the invention.

20 The examples which follow are intended to illustrate the invention in detail, but without restricting it.

Examples:

25 Example 1: Anionic surfactant additive screening

40 g of D,L-methionine and 360 g of water were charged in a flask and circulated via a heat exchanger by pumping at a temperature of 40°C. A solution of 125 g of D,L-methionine in 1125 g of water, heated to 90°C, was added to this suspension at a rate of 18 ml/min, wherein the temperature of the suspension charged was
30 maintained at 40°C. After addition of 650 ml of the hot solution, 500 ml of suspension

were removed and then a further 500 ml of the hot solution were added at a rate of 18 ml/min. The resulting suspension was drained off, the amount of foam determined in ml, and the D,L-methionine was filtered off and washed with 300 ml of acetone. After drying the D,L-methionine, the bulk density was determined.

- 5 For the experiments with NH_3 , the desired concentration was calculated as NH_4^+ concentration and was adjusted in both start solutions/suspensions. Additionally, the amount of methionine was increased by an amount equimolar to the amount of added NH_3 .

10 The crystallization experiments were carried out in the presence of the following additives, where the stated concentration was adjusted by addition of the additive in both start solutions/suspensions.

Additive 1

15 An aqueous mixture comprising 6.9% by weight of silicone oil with a kinematic viscosity of $1000 \text{ mm}^2/\text{s}$ (AK 1000, Wacker-Chemie GmbH), 0.27% by weight of hydrophobized silica (Sipernat D10, Evonik Degussa GmbH) and 17.9% by weight of a polyethoxylated fatty acid mixture (Intrasol® FS 18/90/7, Ashland Deutschland GmbH) was used as pure defoamer 1 (additive 1, comparative example).

The pure crystallization additives used were the following anionic surfactants:

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Additive 2) $\text{C}_n\text{H}_{2n+1}\text{-O-SO}_3\text{Na}$, where $n = 12$ to 18 Sulfopon® 1218G, Oleochemicals)

Additive 3) $\text{C}_n\text{H}_{2n+1}\text{-O-C}_2\text{H}_4\text{-SO}_3\text{Na}$, where $n = 8$ to 18 (Hostapon® SCI 85, Clariant)

Additive 4) $\text{C}_n\text{H}_{2n+1}\text{-(OC}_2\text{H}_4)_2\text{-O-SO}_3\text{Na}$, where $n = 12$ (Disponil® FES 27, Cognis)

25 Comparative Example, additive 5) $\text{C}_n\text{H}_{2n+1}\text{-(OC}_2\text{H}_4)_{12}\text{-O-SO}_3\text{Na}$, where $n = 12$ (Disponil® FES 993, Cognis)

Comparative Example, additive 6) $\text{C}_n\text{H}_{2n+1}\text{-(OC}_2\text{H}_4)_{30}\text{-O-SO}_3\text{Na}$, where $n = 12$ (Disponil® FES 77, Cognis)

For the combination of the crystallization additives with a defoamer, an aqueous mixture 7 was used comprising 6.1% by weight of silicone oil with a kinematic viscosity of 1000 mm²/s (AK 1000, Wacker Chemie GmbH), 0.25% by weight of hydrophobized silica (Sipernat D10, Evonik Degussa GmbH), 2.6% by weight of a polyethoxylated fatty acid mixture (Intrasol® FS 18/90/7, Ashland Deutschland GmbH), 3.7% by weight of a polyethoxylated fatty alcohol mixture (2.35% by weight of Marlupal®, Sasol Germany GmbH, 1.35% by weight of Brij C2, Croda Chemicals Europe) in water (corresponds to 12.65% by weight of active ingredient).

This mixture was used in each case with 5.1% by weight of the corresponding crystallization additive (2, 3 or 4) in water (corresponds to 17.75% by weight of total active ingredient, made up to 100% by weight with water). The following additives were used:

Additive 8) = (7) + (2)

Additive 9) = (7) + (3)

Additive 10) = (7) + (4)

The ratio of defoamer 7: crystallization additive (2, 3, 4) was 2.5:1 (based on the active ingredient) in each case. The concentration data in Table 1 gives the total active ingredient content of the additive without water based on the total mass of the solution or suspension.

Table 1:

Additive	Additive concentration (ppm) ¹⁾	NH ₄ ⁺ concentration (g/kg) ¹⁾	Amount of foam (ml)	D,L-Methionine bulk density (g/l)
None	-	-	550	453
1 (Comparative example)	800	1	20-30	454
2	800	2.5	85	564
3	800	2.5	400	573
4	800	2.5	250	588
5 (Comparative example)	800	2.5	800	492

6 (Comparative example)	800	2.5	1000	463
8	800	2.5	0	630
9	800	2.5	0	634
10	800	2.5	20-30	630

¹⁾in the solution and/or suspension (analogously to Example 1)

Example 2: Influence of the NH_4^+ concentration on the bulk density of methionine

40 g of methionine and 360 g of water were charged in a flask and circulated via a heat exchanger by pumping at a temperature of 40°C. A solution of 125 g of methionine in 1125 g of water, heated to 90°C, was added to this suspension at a rate of 18 ml/min, wherein the temperature of the suspension charged was maintained at 40°C. After addition of 650 ml of the hot solution, 500 ml of suspension were removed and then a further 500 ml of the hot solution were added at a rate of 18 ml/min. The resulting suspension was drained off, the amount of foam determined, and the methionine was filtered off and washed with 300 ml of acetone. After drying the methionine, the bulk density was determined.

For the experiments with NH_3 , the desired concentration was calculated as NH_4^+ concentration and was adjusted in both start solutions/suspensions by addition of aqueous NH_3 solution.

The crystallization experiments were carried out in the presence of additive 8 (according to Example 1), wherein the stated concentration was adjusted by addition of the additive likewise in both start solutions/suspensions according to Table 2.

The concentration data in Table 2 give the total active ingredient content of the additive without water based on the total mass of the solution or suspension.

Table 2:

No.	Additive	Additive concentration (ppm) ¹⁾	NH_4^+ concentration (g/kg) ¹⁾	Amount of foam (ml)	D,L-Methionine bulk density (g/l)
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1	None (comparison)	-	-	350	434
2	8 (comparison)	800	-	200	220
3	8 (comparison)	800	0.25	0	420
4	8 (comparison)	800	0.5	0	505
5	8	800	1	0	586
6	8	800	2.5	0	615

¹⁾in the solution and/or suspension (analogously to Example 1)

Example 3: Nonionic surfactant

48 g of D,L-methionine, 348 g of water and 3.8 g of aqueous NH₃ solution (25%) and 0.32 g of Tween 65 were charged in a flask and circulated via a heat exchanger by pumping at a temperature of 40°C. A solution of 151 g of D,L-methionine, 1087 g of water, 11.8 g of aqueous NH₃ solution (25%) and 1.0 g of Tween 65, heated to 90°C, was added to this suspension at a rate of 18 ml/min, wherein the temperature of the suspension charged was maintained at 40°C. After addition of 650 ml of the hot solution, 500 ml of suspension were removed and then a further 500 ml of the hot solution were added at a rate of 18 ml/min. The resulting suspension was drained off, the amount of foam determined, and the D,L-methionine was filtered off and washed with 300 ml of acetone. After drying the D,L-methionine, the bulk density was determined.

0 ml of foam occurred and the bulk density of the isolated D,L-methionine was 578 g/l.

Example 4: Concentration-dependent experiments

48 g of D,L-methionine, 348 g of water and 3.8 g of aqueous NH₃ solution (25%) were charged in a flask and circulated via a heat exchanger by pumping at a temperature of 40°C. A solution of 151 g of D,L-methionine, 1087 g of water and 11.8 g of aqueous NH₃ solution (25%), heated to 90°C, was added to this suspension at a rate of 18 ml/min, wherein the temperature of the suspension charged was

maintained at 40°C. After addition of 650 ml of the hot solution, 500 ml of suspension were removed and then a further 500 ml of the hot solution were added at a rate of 18 ml/min. The resulting suspension was drained off, the amount of foam determined, and the D,L-methionine was filtered off and washed with 300 ml of acetone. After drying the D,L-methionine, the bulk density was determined.

The crystallization experiments were carried out in the presence of additives 8, 9 or 10 below (according to Example 1), wherein the stated concentration was adjusted by addition of the additive in both start solutions/suspensions according to Table 4.

Additive 8) (7) + (2)

Additive 9) (7) + (3)

Additive 10) (7) + (4)

The concentration data in Table 3 give the total active ingredient content of the additive without water based on the total mass of the solution or suspension.

Table 3:

No.	Additive	Additive concentration (ppm) ¹⁾	Amount of foam (ml)	D,L-Methionine bulk density (g/l)
1	8	100	350	522
2	8	200	180	561
3	8	400	5	610
4	8	800	0	630
5	8	1200	0	624
6	8	2000	0	615
7	8	4000	0	616
8	9	100	450-500	529
9	9	200	200	585
10	9	400	20-30	625
11	9	800	0	634
12	9	1200	0	657
13	9	2000	0	630
14	9	4000	0	601
15	10	100	350	507
16	10	200	150	558
17	10	400	80	614

18	10	800	20-30	630
19	10	1200	20-30	652
20	10	2000	5-10	650
21	10	4000	0	636

¹⁾in the solution and/or suspension (analogously to Example 1)

It can be seen that the additives according to the invention (with defoamer) over the concentration range of 400 to 4000 ppm improve the bulk density of the D,L-

5 methionine to values > 600 g/l.

Claims

1. A method for crystallizing D,L-methionine from aqueous solutions and/or suspensions containing D,L-methionine and D,L-methionine ammonium salt, having a Met content of 70 – 180 g/kg of solution and/or suspension, preferably 90 – 150 g/kg of solution and/or suspension, an NH_4^+ content of 1 – 5 g/kg of solution and/or suspension, in the presence of a crystallization additive,
which comprises a nonionic or anionic surfactant or a mixture of various nonionic or anionic surfactants,
in which the temperature of the solution and/or suspension is lowered directly or stepwise from $T_1 = 85 - 110^\circ\text{C}$ to $T_2 = 30 - 50^\circ\text{C}$, so that D,L-methionine precipitates as a solid.

2. The method as claimed in claim 1, characterized in that the anionic surfactant used for the formation of the crystallization additive is one of the compounds depicted in formulae 1 to 3 or a mixture thereof:



wherein n is an integer from 1 to 10, M is sodium or potassium and R^1 , R^2 and R^3 are a linear, branched or cyclic, saturated or unsaturated C_8 - to C_{20} -alkyl group or an aryl group.

3. The method as claimed in claim 2, characterized in that n is equal to 2 and R^1 , R^2 and R^3 are linear, saturated C_8 - to C_{18} -alkyl groups.

4. The method as claimed in claim 2 or 3, characterized in that $\text{C}_n\text{H}_{2n+1}\text{-O-SO}_3\text{Na}$, where $n = 12$ to 18,

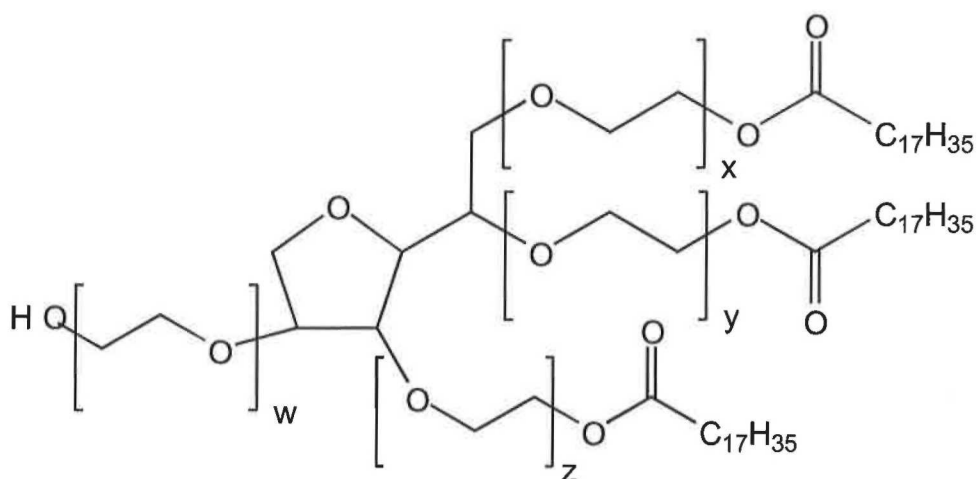
$C_nH_{2n+1}-O-C_2H_4-SO_3Na$, where $n = 8$ to 18 or

$C_nH_{2n+1}-(OC_2H_4)_2-O-SO_3Na$, where $n = 12$

are used as anionic surfactant.

5 5. The method as claimed in claim 1, characterized in that the nonionic crystallization additive is a sorbitan fatty acid ester or a mixture of various sorbitan fatty acid esters.

10 6. The method as claimed in claim 5, characterized in that the sorbitan fatty acid ester according to formula 4



is used,

wherein $w+x+y+z=20$.

15 7. The method as claimed in any of claims 1 to 6, characterized in that the concentration of the crystallization additive in the solution and/or suspension from which the crystallization takes place is at least 700 ppm and not more than 4000 ppm, based on the total mass of the solution and/or suspension, preferably at least 750 ppm and not more than 2000 ppm, particularly
20 preferably at least 800 ppm and not more than 1000 ppm.

8. The method as claimed in any of claims 1 to 5, characterized in that the solution from which the crystallization takes place additionally comprises a defoamer.
- 5 9. The method as claimed in claim 6, characterized in that the defoamer comprises silicone oil.
10. The method as claimed in claim 8 or 9, characterized in that the weight ratio of defoamer: crystallization additive, based on the active ingredient, is in the
10 range of 4:1 to 1:1, preferably in the range of 3:1 to 2:1 and in this case the concentration of the crystallization additive is at least 50 ppm and not more than 1200 ppm, based on the total mass of the solution and/or suspension, preferably 100 ppm to 600 ppm, particularly preferably 200 ppm to 400 ppm.
- 15 11. The method as claimed in any of claims 1 to 10, characterized in that the crystallization takes place by introducing an aqueous solution and/or suspension containing D,L-methionine and D,L-methionine ammonium salt heated to 85 to 110°C into an aqueous solution and/or suspension containing D,L-methionine and D,L-methionine ammonium salt warmed to 30 to 50°C,
20 wherein the temperature of the resulting mixture is constantly maintained between 30 and 50°C.
12. The method as claimed in claim 11, characterized in that the crystallization takes place by introducing a solution containing D,L-methionine and D,L-
25 methionine ammonium salt heated to 85 to 110°C into a suspension containing D,L-methionine and D,L-methionine ammonium salt warmed to 30 to 50°C.
13. The method as claimed in any of claims 1 to 10, characterized in that the
30 crystallization is carried out in two stages, wherein, in the first crystallization

stage, a solution and/or suspension containing D,L-methionine and D,L-methionine ammonium salt heated to 85 to 110°C is introduced into a suspension containing D,L-methionine and D,L-methionine ammonium salt warmed to 60 to 80°C and the temperature of the resulting mixture is constantly maintained between 60 and 80°C and wherein the suspension containing D,L-methionine and D,L-methionine ammonium salt warmed to 60 to 80°C obtained in the first crystallization stage is introduced in a second crystallization stage into a suspension containing D,L-methionine and D,L-methionine ammonium salt warmed to 30 to 50°C, wherein the temperature of the resulting mixture is constantly maintained between 30 and 50°C.

14. The method as claimed in any of claims 1 to 13, characterized in that the crystallization is carried out by vacuum crystallization, wherein the pressure in the crystallization stage is 60 to 1000 mbar and, if a two-stage crystallization is carried out, the pressure in the second crystallization stage is 35 to 200 mbar.

15. The method as claimed in any of claims 1 to 14, characterized in that the aqueous solutions and/or suspensions containing D,L-methionine and D,L-methionine ammonium salts were prepared beforehand by dissolving and/or suspending D,L-methionine in water in the presence of appropriate amounts of ammonia.

16. The method as claimed in claim 15, characterized in that D,L-methionine having a methionine content of at least 90% by weight, preferably at least 95% by weight, is used for the dissolution.

17. The method as claimed in claim 16, characterized in that D,L-methionine is used in the form of pure methionine and/or crude methionine from any manufacturing process having a residual moisture of 0.1 to 9.5% by weight, preferably 0.2 to 4.5% by weight.

18. A method for preparing D,L-methionine, in which an aqueous solution of D,L-methionine ammonium salt is initially formed by hydrolysis of D,L-methionine nitrile and/or D,L-methionine amide, and an aqueous solution and/or suspension containing D,L-methionine and D,L-methionine ammonium salt is produced therefrom by partial removal of the ammonia from the D,L-methionine ammonium salt, from which methionine is then produced by crystallization as claimed in any of claims 1 to 17.
19. The method as claimed in claim 18, characterized in that the aqueous solution of D,L-methionine ammonium salt is brought to an NH_4^+ content of 1 – 5 g/kg of solution and/or suspension, preferably 1.5 to 3.0 g/kg, by evaporating and/or stripping off of ammonia prior to the crystallization.
20. The method as claimed in claim 18 or 19, characterized in that the aqueous solution and/or suspension of D,L-methionine and D,L-methionine ammonium salt is brought to a Met content of 70 – 180 g/kg of solution and/or suspension, preferably 90 to 150 g/kg, by addition of water and/or D,L-methionine.
21. The method as claimed in any of claims 1 to 20, characterized in that the precipitated D,L-methionine is separated from the mother liquor and dried or is initially recrystallized and is dried after separation from the mother liquor obtained in this case.
22. The method as claimed in claim 21, characterized in that the mother liquor is fed back into a crystallization stage.