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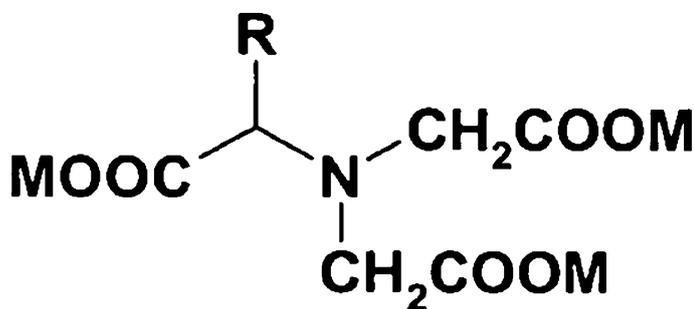
— mit internationalem Recherchenbericht (Artikel 21 Absatz 3)

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[Fortsetzung auf der nächsten Seite]

(54) Title: METHOD FOR PRODUCING A CRYSTALLINE SOLID FROM GLYCINE-N, N-DIACETIC ACID DERIVATIVES

(54) Bezeichnung : VERFAHREN ZUR HERSTELLUNG EINES KRISTALLINEN FESTSTOFFES AUS GLYCIN-N, N-DIESSIGSÄURE-DERIVATEN



(I)

(57) Abstract: The invention relates to a method for producing a crystalline solid from glycine-N,N- diacetic derivatives (e.g. MGDA) with sufficiently reduced hygroscopicity, characterised in that at least one crystalline compound of formula (I) is provided as germ, and a spray granulation is produced with at least one compound of formula (I), preferably followed by a heat treatment.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft ein Verfahren zur Herstellung eines kristallinen Feststoffes aus Glycin-N, N-diessigsäure-Derivaten (z.B. MGDA) mit hinreichend geringer Hygroskopizität, das dadurch gekennzeichnet ist, dass mindestens eine kristalline Verbindung der Formel (I) als Keim vorgelegt wird, und eine Sprühgranulation mit mindestens einer Verbindung der Formel (I) durchgeführt wird, vorzugsweise gefolgt von einer Wärmebehandlung.



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5 **Method for producing a crystalline solid from glycine-N,N-**
 diacetic acid derivatives with sufficiently reduced
 hygroscopicity

10 Complexing agents for alkaline earth metal ions and heavy
metal ions, of the kind used in detergents, for example, are
typically synthesized in aqueous solution. For certain
applications they are required in solid form.

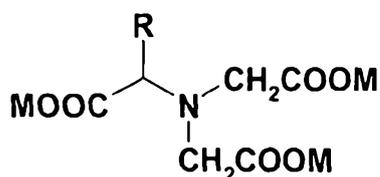
15 Typical processes for producing solids from solutions are, in
particular, crystallization processes and spray drying
processes. It is known that crystalline solid of the kind
produced, for example, in evaporative or cooling
crystallization processes may contain water of crystallization
and under ambient conditions is usually less hygroscopic and
20 more storage-stable than amorphous solid. Through spray drying
processes (e.g., in a spraying tower or in a fluidized
spraying bed), in contrast, the solid is obtained in amorphous
form. In this form the solid is often highly hygroscopic and
when stored in the open under ambient conditions it loses its
25 capacity for free flow within a short time. In the literature,
therefore, measures are described for increasing the storage-
stability of sprayed powders, an example being the compacting
or aftertreatment of builders for laundry detergents with
benzoic acid in US 3,932,316.

30 Glycine-N,N-diacetic acid derivatives as complexing agents for
alkaline earth metal ions and heavy metal ions in a wide
variety of industrial application fields are known from
WO 94/29421. These glycine-N,N-diacetic acid derivatives, an
35 example being α -alanine-N,N-diacetic acid (MGDA) in the form
of the trisodium salt, are highly inhibited in their

5 crystallization, and so typical crystallization processes are impossible or uneconomic. The aftertreatment of amorphous sprayed powders of these compounds with additives, as for example benzoic acid in accordance with US 3,932,316, is undesirable for certain applications, and may also only
10 improve the storage-stability to a limited extent. The stability of a crystalline solid is not attained.

It was an object of the present invention, therefore, to provide a virtually nonhygroscopic, stable, preferably
15 crystalline solid substantially comprising glycine-N,N-diacetic acid derivatives which is largely free from additives.

The present invention relates to a process for preparing a
20 preferably crystalline solid preferably having, for processing and application, for example, a sufficiently low hygroscopicity and substantially comprising glycine-N,N-diacetic acid derivatives of the general formula I

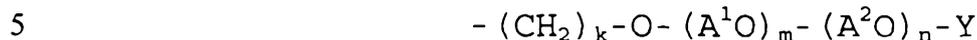


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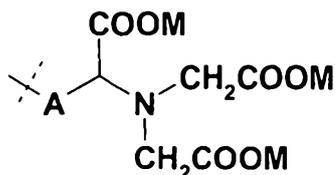
(I)

in which

R is C₁ to C₃₀ alkyl or C₂ to C₃₀ alkenyl, which may additionally carry as substituents up to 5 hydroxyl groups,
30 formyl groups, C₁ to C₄ alkoxy groups, phenoxy groups or C₁ to C₄ alkoxy carbonyl groups and may be interrupted by up to 5 nonadjacent oxygen atoms, alkoxylate moieties of the formula



in which A^1 and A^2 independently of one another denote 1,2-alkylene groups having 2 to 4 C atoms, Y is hydrogen, C_1 to C_{12} alkyl, phenyl or C_1 to C_4 alkoxy carbonyl, and k is the number
 10 1, 2 or 3, and also m and n are each numbers from 0 to 50, the sum of $m + n$ necessarily being at least 4, phenylalkyl groups having 1 to 20 C atoms in the alkyl, a five- or six-membered, unsaturated or saturated, heterocyclic ring having up to three heteroatoms from the group consisting of nitrogen, oxygen, and
 15 sulfur, which may additionally be benzofused, it being possible for all phenyl rings and heterocyclic rings in the definitions for R additionally to carry as substituents up to three C_1 to C_4 alkyl groups, hydroxyl groups, carboxyl groups, sulfo groups or C_1 to C_4 alkoxy carbonyl groups, or is a radical
 20 of the formula



where A denotes a C_1 to C_{12} alkylene bridge or a chemical bond, and
 25 each M independently of any other is hydrogen, alkali metal, alkaline earth metal, ammonium or substituted ammonium (e.g., organic amine salts) in the corresponding stoichiometric amounts,
 which is characterized in that at least one crystalline
 30 compound of the formula I is introduced as seed, and a spray granulation (preferably in a granulator) is carried out with at least one compound of the formula I.

5 Particularly preferred compounds of the formula I are those as described in DE 196 49 681.

In an inherently typical way, in a spray granulation, small to ultra small droplets in the region of 50 μm of a liquid
10 sprayed through nozzles are dried in a reaction chamber, by direct heat transfer in a warm or hot air stream to form particles. From aqueous solutions, emulsions or dispersions, for example, ultra small particles (seeds) are first produced in the reaction chamber through drying of these sprayed
15 droplets (alternatively, these seeds may also be introduced at the start). These seeds are held in a state of suspension (fluidization) in a fluidized bed, and form the surface for layerwise adsorption and drying of further sprayed droplets. The particles thus produced can be removed continuously from
20 the drying chamber without interruption to the drying procedure by means of a classifying discharge in a flexible way - for example, with freely adjustable particle sizes. On the process of spray granulation, see also H. Uhlemann, L. Mörl, "Wirbelschicht - Sprühgranulation" Springer-Verlag
25 2000 (ISBN 3-540-66985-X).

The process of the present invention is characterized in that at least one preferably crystalline compound of the formula I is introduced in the form of seeds and then in an inherently
30 typical way a spray granulation is carried out with at least one compound of the formula I, preferably in solution (more particularly in aqueous solution, e.g., about 40% strength).

A spray granulation is carried out preferably with the
35 following parameters:

5 Preferred air feed temperature: 90-160°C, preferred air departure temperature: 40-110°C, preferred product temperature: 40-110°C, preferred spraying air temperature: 70-110°C, preferred spraying air pressure: 1-6 bar, preferred spraying solution temperature: 50-95°C.

10

In the process of the invention, for example, liquid raw material (e.g., a 40% strength aqueous solution of a compound of the formula I) is sprayed onto the crystal seeds (of compounds of the formula I) in fluid motion in the hot air stream, and thereby dries and causes the seeds to grow. This procedure is preferably operated continuously, with preferably continuous removal of a portion of the product from the granulator, followed by its treatment with an additional tempering step (heat-treatment step). This lowers the hygroscopicity of the product, preferably by raising the crystalline fraction in the product. The product thus treated represents the end product, and in turn preferably a portion is ground and introduced as new seeds back into the granulator.

25

The product is preferably heat-aftertreated (tempered) with the following temperature profile: beginning with a bed temperature of 50-90°C, the bed temperature is raised to 90-130°C over the course of about an hour, and then held at this temperature for about 60 minutes.

30

The granulator is preferably a fluid-bed spray granulator which is equipped, for example, with a cyclone and/or a filter.

35

5 With the process of the present invention, it is necessary preferably only right at the beginning to introduce crystalline product, after which a spray granulation (which without introduction of crystalline product would only produce far more amorphous granules, for example) and the subsequent
10 tempering (heat-treatment) results persistently in a product having a relatively high crystalline fraction (and, consequently, substantially lower hygroscopicity).

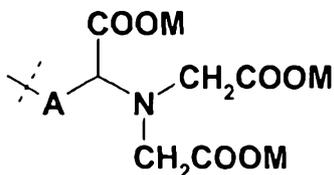
The expression "crystalline" relates preferably to a
15 crystalline fraction of at least 60% by weight.

A solid is said here to be nonhygroscopic or of sufficiently low hygroscopicity when on storage in the open under normal ambient conditions, e.g., 25°C and a relative humidity of 76%,
20 it preserves its consistency as (preferably free-flowing) powder or granules over a period of at least one day, preferably one week.

The preferably crystalline solid prepared in accordance with
25 the invention substantially comprises compounds of the formula I, and small amounts of starting products and/or by-products from the preparation of the glycine-N,N-diacetic acid derivatives I may additionally be present. Typical purities for the compounds I, depending on the synthesis process
30 employed, are 70% to 99.9% by weight, more particularly 80% to 99.5% by weight, based in each case on the solids content.

The crystalline starting substance may be prepared, for example, by the process described in DE 196 49 681.

5 The process of the invention is suitable preferably for those compounds I in which R is C₁ to C₂₀ alkyl, C₂ to C₂₀ alkenyl or a radical of the formula



10

As compound I it is particularly preferred to use α -alanine-N,N-diacetic acid (R = CH₃, MGDA) and its salts. It is preferred, for example, to use its alkali metal salts, ammonium salts, and substituted ammonium salts.

15

Suitable such salts are in particular the sodium, potassium, and ammonium salts, more particularly the trisodium, tripotassium, and triammonium salt, and also organic triamine salts with a tertiary nitrogen atom.

20

Suitable bases as a parent to the organic amine salts are, in particular, tertiary amines, such as trialkylamines having 1 to 4 C atoms in the alkyl, such as trimethylamine and triethylamine, and trialkanolamines having 2 or 3 C atoms in the alkanol residue, preferably triethanolamine, tri-n-propanolamine or triisopropanolamine.

The calcium salts and magnesium salts are used in particular as alkaline earth metal salts.

30

Besides methyl, straight-chain or branched alk(en)yl radicals contemplated for the radical R include in particular C₂ to C₁₇

5 alkyl and alkenyl, more particularly straight-chain radicals derived from saturated or unsaturated fatty acids.

Examples of individual radicals R are as follows: ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl,
10 n-pentyl, isopentyl, tert-pentyl, neopentyl, n-hexyl, n-heptyl, 3-heptyl (derived from 2-ethylhexanoic acid), n-octyl, isooctyl (derived from isononanoic acid), n-nonyl, n-decyl, n-undecyl, n-dodecyl, isododecyl (derived from isotridecanoic acid), n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-
15 heptadecyl, n-octadecyl, n-nonadecyl, n-eicosyl and n-heptadecenyl (derived from oleic acid). For R it is also possible for mixtures to occur, more particularly those which derive from naturally occurring fatty acids and from synthetically produced technical acids, as a result of oxo-
20 process synthesis, for example.

Serving as C_1 to C_{12} alkylene bridges A are, in particular, polymethylene moieties of the formula $(CH_2)_k$, in which k denotes a number from 2 to 12, more particularly from 2 to 8,
25 i.e., 1,2-ethylene, 1,3-propylene, 1,4-butylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, nonamethylene, decamethylene, undecamethylene and dodecamethylene. Hexamethylene, octamethylene, 1,2-ethylene and 1,4-butylene are particularly preferred in this context.
30 In addition, however, branched C_1 to C_{12} alkylene groups may also occur, e.g., $-CH_2CH(CH_3)CH_2-$, $-CH_2C(CH_3)_2CH_2-$, $-CH_2CH(C_2H_5)-$, or $CH_2CH(CH_3)-$.

The C_1 to C_{30} alkyl and C_2 to C_{30} alkenyl groups may carry up to
35 5, more particularly up to 3, additional substituents of the stated type, and may be interrupted by up to 5, more

5 particularly up to 3, nonadjacent oxygen atoms. Examples of such substituted alk(en)yl groups are $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3$, $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3$, $-\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$, $-\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{OH}$, $-\text{CH}_2-\text{CHO}$, $-\text{CH}_2-\text{OPh}$, $-\text{CH}_2-\text{COOCH}_3$ or $-\text{CH}_2\text{CH}_2-\text{COOCH}_3$.

10

Alkoxyate moieties contemplated include in particular those in which m and n are each independently of one another numbers from 0 to 30, especially from 0 to 15. A^1 and A^2 preferably denote groups derived from butylene oxide and especially groups derived from propylene oxide and from ethylene oxide. Of particular interest are pure ethoxylates and pure propoxylates, although ethylene oxide-propylene oxide block structures may also occur.

20 As five- or six-membered, unsaturated or saturated, heterocyclic rings having up to three heteroatoms from the group consisting of nitrogen, oxygen, and sulfur, which may additionally be benzofused and may be substituted by the designated radicals, the following are contemplated:

25 tetrahydrofuran, furan, tetrahydrothiophene, thiophene, 2,5-dimethylthiophene, pyrrolidine, pyrroline, pyrrole, isoxazole, oxazole, thiazole, pyrazole, imidazoline, imidazole, 1,2,3-triazolidine, 1,2,3- and 1,2,4-triazole, 1,2,3-, 1,2,4- and 1,2,5-oxadiazole, tetrahydropyran, dihydropyran, 2H- and 4H-
30 pyran, piperidine, 1,3- and 1,4-dioxane, morpholine, pyrazan, pyridine, α -, β - and γ -picoline, α - and γ -piperidone, pyrimidine, pyridazine, pyrazine, 1,2,5-oxathiazine, 1,3,5-, 1,2,3- and 1,2,4-triazine, benzofuran, thionaphthene, indoline, indole, isoindoline, benzoxazole, indazole,
35 benzimidazole, chroman, isochroman, 2H- and 4H-chromene, quinoline, isoquinoline, 1,2,3,4-tetrahydroisoquinoline,

5 cinnoline, quinazoline, quinoxaline, phthalazine, and benzo-
1,2,3-triazine.

N-H moieties in the stated heterocyclic rings ought as far as
possible to be in derivatized form, for instance as an N-alkyl
10 moiety.

In the case of substitution on the phenyl rings or the
heterocyclic rings, there are preferably two (identical or
different) or, more particularly, one individual substituent
15 present.

Examples of optionally substituted phenylalkyl groups and
alkyl groups which carry heterocyclic rings, for R, are
benzyl, 2-phenylethyl, 3-phenylpropyl, 4-phenylbutyl, o-, m-
20 or p-hydroxybenzyl, o-, m- or p-carboxybenzyl, o-, m- or p-
sulfobenzyl, o-, m- or p-methoxy- or -ethoxycarbonylbenzyl, 2-
furylmethyl, N-methylpiperidin-4-ylmethyl or 2-, 3- or 4-
pyridinylmethyl.

25 In the case of substitution on phenyl rings and also on
heterocyclic rings, the groups in question are preferably
groups conferring solubility in water, such as hydroxyl
groups, carboxyl groups or sulfo groups.

30 The radicals listed above for R should also be understood
correspondingly, to be examples of the stated C₁ to C₄, C₁ to
C₁₂, and C₁ to C₂₀ alkyl groups.

The crystalline solid prepared in accordance with the
35 invention is especially suitable as a component for solid
detergent formulations. In addition, therefore, solid

5 detergent formulations which comprise the crystalline solid of
sufficiently low hygroscopicity, prepared in accordance with
the invention, comprising glycine-N,N-diacetic acid
derivatives I, as complexing agent for alkaline earth metal
ions and heavy metal ions, in the amounts customary for this
10 purpose, in addition to other customary ingredients of such
formulations, are also provided by the present invention.
Compositions and customary ingredients of solid detergent
formulations of this kind are known to the skilled person and
therefore need not be elucidated in any more detail here.

15

The example below is intended to elucidate the invention in
more detail. The glycine-N,N-diacetic acid derivative I used
was α -alanine-N,N-diacetic acid (methylglycine-N,N-diacetic
acid, "MGDA"), trisodium salt.

20

Example

The procedure below was carried out in a fluid-bed spray
granulator which is equipped with a cyclone, a filter, and a
25 gas scrubber.

The starting material (Trilon[®] M, liquid, from BASF AG) was
heated to 90°C with continuous and intense mixing and was used
at this temperature for the granulation. Under the following
30 conditions, a stable granulating operation was achieved:

Process parameters:	
Feed air temperature	125°C
Departing air temperature	65°C
Product temperature	65 - 70°C
Intake air volume	1300 m ³ /h

Spraying air temperature	90°C
Spraying air pressure	3 bar
Spraying solution temperature	80°C

5

In order to raise the crystallinity, the product prepared was aftertreated with a temperature profile commencing with a bed temperature of 70°C, then raising this temperature to around 110 - 120°C over the course of around an hour, and subsequently holding at this temperature for around 60 minutes.

10 Screening at 1000 microns and re-use of the ground coarse material as crystallization seeds for the granulation process led to a stable operation with a yield of about 20 kg of granules per hour in the desired quality. The introduction of comminuted material was advantageous for the process, in order to maintain the height of the bed, and in order to obtain the product in a crystalline form.

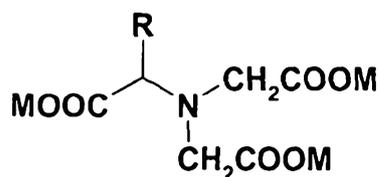
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Claims

1. A process for preparing a crystalline solid substantially comprising glycine-N,N-diacetic acid derivatives of the general formula I

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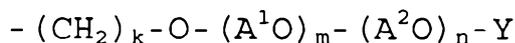
(I)

in which

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R is C₁ to C₃₀ alkyl or C₂ to C₃₀ alkenyl, which may additionally carry as substituents up to 5 hydroxyl groups, formyl groups, C₁ to C₄ alkoxy groups, phenoxy groups or C₁ to C₄ alkoxy carbonyl groups and may be interrupted by up to 5 nonadjacent oxygen atoms, alkoxy moieties of the formula

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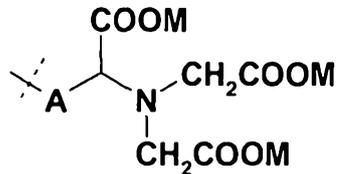


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in which A¹ and A² independently of one another denote 1,2-alkylene groups having 2 to 4 C atoms, Y is hydrogen, C₁ to C₁₂ alkyl, phenyl or C₁ to C₄ alkoxy carbonyl, and k is the number 1, 2 or 3, and also m and n are each numbers from 0 to 50, the sum of m + n necessarily being at least 4, phenylalkyl groups having 1 to 20 C atoms in the alkyl, a five- or six-membered, unsaturated or saturated, heterocyclic ring having up to three heteroatoms from the group consisting of nitrogen, oxygen, and sulfur, which may additionally be benzofused, it being possible for all phenyl rings and heterocyclic rings in the definitions for

30

5 R additionally to carry as substituents up to three C₁ to C₄ alkyl groups, hydroxyl groups, carboxyl groups, sulfo groups or C₁ to C₄ alkoxy carbonyl groups, or is a radical of the formula



10

where A denotes a C₁ to C₁₂ alkylene bridge or a chemical bond, and

each M independently of any other is hydrogen, alkali metal, alkaline earth metal, ammonium or substituted ammonium in the corresponding stoichiometric amounts,

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wherein at least one crystalline compound of the formula I is introduced, and a spray granulation is carried out with at least one compound of the formula I.

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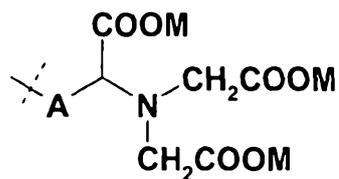
2. The process according to claim 1, wherein part of the product is removed from the granulator, ground, and introduced as new seeds into the granulator.

25

3. The process according to claim 1 or 2, wherein an aqueous solution of a compound of the formula I is used for the spray granulation.

30

4. The process according to claims 1 to 3 for preparing a crystalline solid of sufficiently low hygroscopicity from glycine-N,N-diacetic acid derivatives I in which R is C₁ to C₂₀ alkyl, C₂ to C₂₀ alkenyl or a radical of the formula



5

5. The process according to claims 1 to 4 for preparing a crystalline solid of sufficiently low hygroscopicity from α -alanine-N,N-diacetic acid (MGDA) or the alkali metal, ammonium or substituted amine salts thereof.
- 10 6. The process according to any of claims 1 to 5, the product being heat-aftertreated.
- 15 7. A solid detergent formulation comprising the crystalline solid, prepared according to claims 1 to 6, of glycine-N,N-diacetic acid derivatives I as complexing agent for alkaline earth metal ions and heavy metal ions.