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## Patent Application

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(54) **Title:**

**METHOD FOR PRODUCING A CRYSTALLINE SOLID  
FROM GLYCINE-N, N-DIACETIC ACID DERIVATIVES WITH  
SUFFICIENTLY REDUCED HYGROSCOPICITY**

(57) **Abstract:**

Abstract Method for producing a crystalline solid from glycine-N, N-diacetic acid derivatives with sufficiently reduced hygroscopicity The present invention relates to a process for preparing a crystalline solid from glycine-N,N-diacetic acid derivatives (e.g., MGDA) of sufficiently low hygroscopicity, which is characterized in that at least one crystalline compound of the formula I in is introduced as seed, and a spray granulation is carried out with at least one compound of the formula I, preferably followed by a heat treatment. No suitable figure

## Abstract

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

5

The present invention relates to a process for preparing a crystalline solid from glycine-N,N-diacetic acid derivatives  
10 (e.g., MGDA) of sufficiently low hygroscopicity, which is characterized in that at least one crystalline compound of the formula I is introduced as seed, and a spray granulation is carried out with at least one compound of the formula I, preferably followed by a heat treatment.

No suitable figure

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.

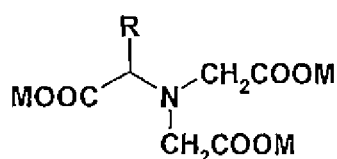
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Glycine-N,N-diacetic acid derivatives as complexing agents for  
alkaline earth metal ions and heavy metal ions in a wide  
variety of industrial application fields are known from  
WO 94/29421. These glycine-N,N-diacetic acid derivatives, an  
35       example being  $\alpha$ -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.

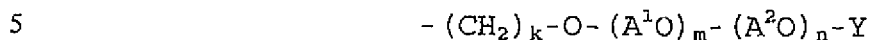
The present invention relates to a process for preparing a  
20 preferably crystalline solid preferably having, for processing and application, for example, a sufficiently low hygroscopicity and substantially comprising glycine-N,N-diacetic acid derivatives of the general formula I



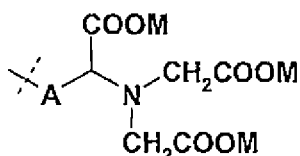
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25 in which

R is C<sub>1</sub> to C<sub>30</sub> alkyl or C<sub>2</sub> to C<sub>30</sub> alkenyl, which may additionally carry as substituents up to 5 hydroxyl groups,  
30 formyl groups, C<sub>1</sub> to C<sub>4</sub> alkoxy groups, phenoxy groups or C<sub>1</sub> to C<sub>4</sub> alkoxycarbonyl groups and may be interrupted by up to 5 nonadjacent oxygen atoms, alkoxylate moieties of the formula



in which  $\text{A}^1$  and  $\text{A}^2$  independently of one another denote 1,2-alkylene groups having 2 to 4 C atoms, Y is hydrogen,  $\text{C}_1$  to  $\text{C}_{12}$  alkyl, phenyl or  $\text{C}_1$  to  $\text{C}_4$  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  $\text{C}_1$  to  $\text{C}_4$  alkyl groups, hydroxyl groups, carboxyl groups, sulfo groups or  $\text{C}_1$  to  $\text{C}_4$  alkoxy carbonyl groups, or is a radical  
 20 of the formula



where A denotes a  $\text{C}_1$  to  $\text{C}_{12}$  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  $\mu\text{m}$  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  
15 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  
20 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  
30 this temperature for about 60 minutes.

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.

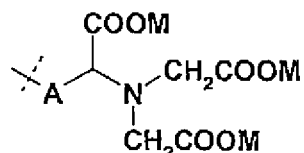
A solid is said here to be nonhygroscopic or of sufficiently low hygroscopicity when on storage in the open under normal ambient conditions, e.g., 25°C and a relative humidity of 76%,  
20 it preserves its consistency as (preferably free-flowing) powder or granules over a period of at least one day, 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 C<sub>1</sub> to C<sub>20</sub> alkyl, C<sub>2</sub> to C<sub>20</sub> alkenyl or a radical of the formula



10

As compound I it is particularly preferred to use α-alanine-N,N-diacetic acid (R = CH<sub>3</sub>, 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.

25

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 C<sub>2</sub> to C<sub>17</sub>

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.  $\text{A}^1$  and  $\text{A}^2$  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-pyran, piperidine, 1,3- and 1,4-dioxane, morpholine, pyrazan, 30 pyridine,  $\alpha$ -,  $\beta$ - and  $\gamma$ -picoline,  $\alpha$ - and  $\gamma$ -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 C<sub>1</sub> to C<sub>4</sub>, C<sub>1</sub> to  
C<sub>12</sub>, and C<sub>1</sub> to C<sub>20</sub> 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  $\alpha$ -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 <sup>3</sup> /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.

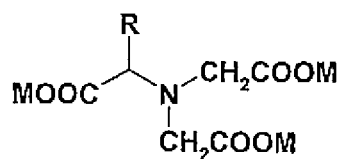
10 Screening at 1000 microns and re-use of the ground coarse material as crystallization seeds for the granulation process led to a stable operation with a yield of about 20 kg of granules per hour in the desired quality. The introduction of  
15 comminuted material was advantageous for the process,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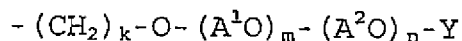
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in which

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R is C<sub>1</sub> to C<sub>30</sub> alkyl or C<sub>2</sub> to C<sub>30</sub> alkenyl, which may additionally carry as substituents up to 5 hydroxyl groups, formyl groups, C<sub>1</sub> to C<sub>4</sub> alkoxy groups, phenoxy groups or C<sub>1</sub> to C<sub>4</sub> alkoxycarbonyl groups and may be interrupted by up to 5 nonadjacent oxygen atoms, alkoxylate moieties of the formula

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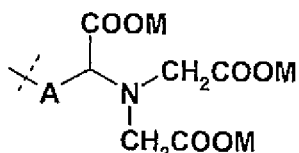


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in which A<sup>1</sup> and A<sup>2</sup> independently of one another denote 1,2-alkylene groups having 2 to 4 C atoms, Y is hydrogen, C<sub>1</sub> to C<sub>12</sub> alkyl, phenyl or C<sub>1</sub> to C<sub>4</sub> alkoxycarbonyl, and k is the number 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 C<sub>1</sub> to C<sub>4</sub> alkyl groups, hydroxyl groups, carboxyl groups, sulfo groups or C<sub>1</sub> to C<sub>4</sub> alkoxy carbonyl groups, or is a radical of the formula



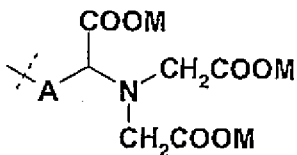
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where A denotes a C<sub>1</sub> to C<sub>12</sub> alkylene bridge or a chemical bond, and

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

- 20 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.
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.
- 25 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 C<sub>1</sub> to C<sub>20</sub> alkyl, C<sub>2</sub> to C<sub>20</sub> alkenyl or a radical of the formula
- 30





5

5. The process according to claims 1 to 4 for preparing a crystalline solid of sufficiently low hygroscopicity from  $\alpha$ -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.