(19) DANMARK

Patent- og Varemærkestyrelsen

(10) **DK/EP 3293165 T3**

(12) Oversættelse af europæisk patentskrift

(51) Int.Cl.: ***C 05 D 9/00 (2006.01)***

(45) Oversættelsen bekendtgjort den: **2024-08-26**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2024-06-26**

(86) Europæisk ansøgning nr.: **17001351.0**

(86) Europæisk indleveringsdag: **2017-08-08**

(87) Den europæiske ansøgnings publiceringsdag: **2018-03-14**

(30) Prioritet: **2016-09-06 DE 102016116633**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

(73) Patenthaver: **Glatt Ingenieurtechnik GmbH, Nordstrasse 12, 99427 Weimar, Tyskland**
Seraplant GmbH, Neuhaldensleber Straße 22A, 39340 Haldensleben, Tyskland

(72) Opfinder: **LEIDOLPH, Lars, Wiesenweg 15, 99438 Bad Berka, Tyskland**
BÖBER, Reinhard, Robert-Koch-Straße 8, 99425 Weimar, Tyskland
JACOB, Michael, Paul-Schneider-Straße 61, 99425 Weimar, Tyskland

(74) Fuldmægtig i Danmark: **Zacco Denmark A/S, Arne Jacobsens Allé 15, 2300 København S, Danmark**

(54) Benævnelse: **Fremgangsmåde til fremstilling af gødningsgranulat, gødningsgranulat**

(56) Fremdragne publikationer:
EP-A1- 3 037 396
EP-A2- 1 918 266
WO-A2-2006/091645
US-A1- 2004 120 867

Method for the production of fertiliser granules; Fertiliser granules

State of the art

The invention is based on a method for producing fertilizer granules according to patent claim 1 and a fertilizer granule according to patent claim 12.

The invention relates to a method for the production of fertilizer granules and to a fertilizer granule, in which method a suspension of phosphate-containing secondary raw materials and mineral acids is produced and this suspension is subsequently fed to a granulation, the fertilizer granules being formed and the P_2O_5 content contained in the fertilizer granules being greater than 75% neutral ammonium citrate soluble.

Phosphorus ores are important sources of raw materials for the production of a wide variety of phosphorus products used in industry and agriculture. Fertilizers and animal feed represent the largest share of global phosphorus consumption. This makes it a very important economic commodity. However, proven global reserves are in sharp decline. As a fertilizer, phosphate cannot be substituted by other substances, which is problematic because intensive agriculture is not possible without phosphate fertilization. For this reason, it is necessary to utilize the large quantities of phosphate that are produced each year as part of various wastes.

There is a whole range of waste, such as municipal sewage sludge, that contains phosphate. However, if the P_2O_5 concentration is too low, this often prevents direct utilization as a phosphate raw material. In the case of ashes from a mono-incineration plant or when the sewage sludge is incinerated with other biogenic waste, however, the phosphate is concentrated. Depending on the sewage sludge used, for example, phosphate concentrations of around 20 % and higher can be achieved. These higher concentrations are economically interesting. However, it is not possible to use such ashes directly as fertilizer, for example, as the important phosphates are converted into a water-insoluble form, i.e. not available to plants, by the combustion process.

In the state of the art, various approaches are known for the utilization or extraction of phosphorus from the ash of mono sewage sludge incineration. For example, direct processing of the ash in the fertilizer industry, washing out the phosphates with hot water and subsequent precipitation or crystallization or elution of the phosphates from the ash with sulphuric acid using ion exchangers. Other well-known methods include the so-called Kepro process, which uses acid and heat to extract phosphate, the Seaborne method, the Phostrip process and the Ashdec method.

Various methods are also known in which the largely insoluble phosphate from phosphate-containing secondary raw materials (such as from sewage sludge ash) is digested using mineral acids, in that the solid phosphate-containing secondary raw materials and the mineral acids are largely mixed directly and fertilizers are produced therefrom. For example, a method for the production of phosphate fertilizers is known from the publication DE 10 2010 034 042 A1, in which a homogeneous mixture is first produced from ash from the mono-incineration of municipal sewage sludge, possibly with the addition of potassium and/or a nitrogen carrier. Once this homogeneous mixture is available, orthophosphoric acid is added to the ongoing mixing process in varying concentrations. The desired conversion reactions and granulation take place essentially simultaneously. The mixing, the reaction and the granulation take place in a mixing apparatus. Ploughshare mixers with a set of blades, a continuously operating continuous mixer or a double-shaft paddle mixer are suggested for this purpose. If necessary, the granules can then be dried further. A known disadvantage of this type of method is that, depending on the type of raw materials, combining the phosphate-containing secondary raw materials and the mineral acid can lead to exothermic reactions, some of which can occur spontaneously and violently. One cause of this is, for example, the presence of free lime in the phosphate-containing secondary raw material, as is typical of sewage sludge ash. Free lime can be contained in sewage sludge ashes in relevant quantities, for example in the range of 10 - 20 %. Consequently, granulation or extrusion methods, in which the solid phosphate-containing secondary raw materials and the mineral acids are extensively mixed directly, result in spontaneous and violent reactions that are difficult to handle and control, depending on the type of raw materials used. Poorly manageable and barely controllable reactions make process control more difficult and thus production with a uniform product quality more difficult, if not completely impossible. Another known disadvantage of this type of method is that the essentially direct mixing of the phosphate-containing secondary raw materials and the diluted or undiluted mineral acid often results in a particularly sticky mixture. This is particularly typical when phosphoric acid is used, as is known, for example, from the publication DE 10 2010 034 042 A1. This sticky mixture is difficult to handle, can only be formed into round granules to a limited extent and often leads to process disruptions due to clogging of narrow passages or excessive adhesion to the surface of system components. Mineral acids are also corrosive. If the mineral acid obtains contact with plant components, a corrosion reaction occurs with these, especially with plant components made of steel, which are typical for such apparatus equipment. This is the case, for example, in granulation or extrusion methods in which the solid phosphate-containing secondary raw materials and the mineral acids are essentially mixed directly. Although measures can be taken here to contain the corrosion, such as a corrosion-resistant coating of the relevant components or apparatus components, such a procedure further increases the investment costs and is therefore expensive, and such a procedure is often only possible to a limited extent and ultimately cannot completely prevent corrosion.

DE 10 2009 020 745 A1 discloses a method for the recovery of valuable substances, in particular phosphate, from sewage sludge products, namely sewage sludge, sewage sludge ash or sewage sludge slag, by extraction, wherein a suspension of the sewage sludge product in water, alcohol, a water/alcohol mixture or an aqueous solution is prepared and gaseous or supercritical carbon dioxide is introduced into this suspension of the sewage sludge product as an extracting agent, undissolved solids are separated from the liquid suspending agent, carbon dioxide is removed from the suspending agent and valuable substances dissolved in the suspending agent are precipitated and separated from the suspending agent. The disadvantage of this method is the very high effort required to carry it out, which makes it very cost-intensive.

From the international patent application with publication number WO 00/50343 A2, a method is known in which incineration ash is digested with sulphuric acid. This produces phosphoric acid. A combination of ion exchanger filters is used to purify the phosphoric acid, whereby a strongly acidic cation exchanger is used in particular to remove iron and heavy metal ions. One of the disadvantages of such a method is the high consumption of chemicals to regenerate the ion exchangers.

Patent specification CH 697 083 A5 discloses a method and a plant for recovering phosphorus from incineration ash containing phosphorus. For this purpose, the phosphates contained in the incineration ash are brought into solution by acid digestion. The digestion solution thus obtained is filtered off from the remaining solids in a filtration device. The filter cake of these solids is disposed of or further processed. The solution is purified and iron and heavy metals in particular are removed. Calcium phosphates are precipitated from the purified raffinate.

DE 102 06 347 A1 discloses a method for recovering phosphorus compounds from incineration residues. For this purpose, diluted mineral acids are added to the incineration ash to dissolve the phosphate compounds contained in the incineration ash, then the phosphate-containing solution is separated from insoluble accompanying components and from non-phosphate-containing parts separated by precipitation, followed by the preparation of the resulting phosphate solution.

A method is known from patent specification EP 2 602 013 B1 in which the phosphorus-containing compounds contained in the sewage sludge ash are brought into solution by acid digestion with a diluted mineral acid. The sewage sludge ash-acid suspension is then separated by filtration into a low-phosphorus filter cake and a phosphorus-rich filtrate. The heavy metal cations that have been dissolved out of the sewage sludge ash are then separated, as they are otherwise incorporated into the phosphorus product precipitated in the last step of the method. This is done by adding a sacrificial metal. The heavy metal mixture deposited in this way is then separated by filtration. An aluminum salt is then added to the filtrate. By adding a base, the pH value is raised to 2.1 to 3.0 and the dissolved phosphorus compounds are essentially completely precipitated in the form of basic aluminum phosphates and separated by filtration. Due to this low precipitation pH value of maximum 3.0, heavy metal cations with a higher precipitation pH value such as cobalt, chromium, iron, manganese, nickel and zinc etc. remain in solution and can be separated from the product. The precipitated phosphorus product, i.e. the aluminium phosphate, can now be used either for fertilizer production or for thermal phosphorus production.

US 2004/0120867 A1 shows a method for improving the nutrient content of organic waste material, such as sewage sludge, by processing it into fertilizer granules. In a first step of the method, a suspension is produced from the organic waste material with water. In the second step, a base and an acid are then added to the suspension in a reaction tank to produce a melt. In a third step, the melt is sprayed onto a fixed bed consisting of fine particles in a granulator in order to evaporate the water in the melt. In the fourth step, the melt reduced by the evaporated water is rolled in the granulator with the fine particles to produce granules. In a further fifth step, the granules are treated with ammonia to complete the product formation reaction. Finally, the ammonia-treated granules are dried in a dryer to obtain fertilizer granules with an improved nutrient content.

The European patent application EP 3 037 396 A1 discloses a method for the production of a phosphate-containing fertilizer from sewage sludge or waste fermentation ashes. The method according to the document comprises 6 steps, wherein in a first step a suspension is produced from a first quantity of ash and a mineral acid in a first vessel. In the second step, a first partial amount of moist solid is separated from the suspension into a second vessel and the remaining mineral acid in the first vessel is mixed with further ash. The separated moist solids produced are collected in the second vessel and purified in two further steps by adding a pH-neutral, basic or buffered aqueous solution, in particular to remove the heavy metal ions contained therein. In the fifth step, the purified, moist solids are separated from the second vessel. Steps 2 to 5 are repeated. It is then possible to dry the moist solids from the second vessel in a post-treatment step.

US 2006/091645 A2 describes a method for the production of fertilizers from organic sludge from municipal sewage treatment plants for pharmaceutical fermentation. In a first step of the method, the organic sludge is stirred by means of a stirring device with a sufficiently large force so that a thixotropic paste is formed, to which an acid is added in a second step of the method. In a third step, the acidic thixotropic paste is mixed with an inorganic high-temperature fertilizer melt, which comprises ammonium salts, at a temperature above 85 °C. Finally, in a fourth step, a hardener is added to the acidic paste in addition to a pH control agent and the water is removed from the paste to obtain the fertilizer.

The problems with the four methods listed above are, on the one hand, the very complex removal of heavy metals and, on the other hand, the fact that the separated filter cake remains as residual or waste material.

From the European patent application EP 1 873 132 A1, a method for the production of combination fertilizers containing phosphate and potash (PK) is known, in which the ash residues obtained from the calcination of chicken droppings are utilized and the phosphate components contained therein are treated with organic acid and a catalyst, an alkaline earth metal compound for reaction control, in order to make them available. It is described that the alkaline earth metal compounds are necessary because the reaction heat of the reaction of the alkaline earth metal compounds and the mineral acid is ultimately required to effectively convert the phosphate phases. After the reaction of ash, alkaline earth compound and mineral acid in the specified ratio, a powder is obtained which can be granulated in a subsequent step. Wet granulation with a granulating plate and subsequent drying are proposed for this purpose. This method therefore requires the use of a catalyst. In order to obtain a granule that can be used in agriculture, it is necessary to produce a powder and then process, granulate and dry it again. All method steps are very complex, which makes the entire proposed method very costly to carry out.

The publication DE 10 2014 005 929 A1 describes a method for the production of phosphorus-containing fertilizer from ash from the mono-incineration of municipal sewage sludge and/or ash from the joint incineration of municipal sewage sludge and animal bone material with diluted orthophosphoric acid with the simultaneous addition of the auxiliary substance calcium hydrogen phosphate, which acts as a catalyst. The reaction of the tertiary calcium compounds and calcium, iron and aluminum silicate compounds contained in the mixture of ash takes place with a special concentration of orthophosphoric acid to form calcium dihydrogen diphosphate. With the calcium hydrogen phosphate acting as a catalyst, the calcium, iron and aluminum silicate compounds are formed into corresponding secondary and/or primary calcium, iron and aluminum silicate dihydrogen phosphate compounds. When hardened with water, calcium silicate hydrate and/or calcium aluminate ferrite fibers grow. The resulting product is ready for pelletizing and is fed to the pelletizing/granulating plate via a buffer container and rolled up into pellets. Pelletizing can be a continuous or discontinuous process. This granule then goes through a drying process to ensure post-drying, which depends on the previous method.

The European patent application EP 1 918 266 A2 discloses a method wherein a fertilizer granulate is produced by first combining the ash residues of the chicken droppings with a potassium component and/or a slag powder and then mixing them with a mineral acid, wherein specific reactions take place between the individual components which convert the poorly soluble phosphates into available components of the fertilizer and the potassium and/or silicon content in the fertilizer increases. The reaction between the potassium component and/or the slag with the acid leads to considerable heat generation due to a neutralization reaction and results in the desired phase transformation of the phosphate from the ash residues of the chicken droppings. The disadvantage of this solution is that without the addition of the potassium component and/or the slag powder, the temperature would not be sufficient to make the phosphate more soluble.

European patent application EP 0 937 694 A1 shows a method for reducing the high pH value resulting from the CaO content in the chicken droppings ash by adding and reacting with a monoammonium salt or a monopotassium metal salt. The disadvantage of this method is that the pH value must first be neutralized by adding monoammonium salt or a monopotassium metal salt so that the method can proceed.

The methods described show the basic and known possibilities of processing phosphate-containing ashes into a phosphate fertilizer, which, however, do not produce the desired results in practice and/or are difficult to implement technically taking into account the economic framework conditions.

The invention is therefore based on the task of providing an economical, ecological, flexible and simple method for the production of fertilizer granules from phosphorus-containing secondary raw materials. By means of this method, phosphate fertilizers and/or complex fertilizers are to be produced in granular form (fertilizer granules), which can be used in agriculture, forestry and horticulture to adjust the nutrient supply for the cultivated crops. The method produces almost no residues.

The task is solved by a method having the features of claim 1, in that a suspension is produced from at least one ash comprising at least one phosphate-containing secondary raw material and at least one mineral acid, the ash comprising the at least one phosphate-containing secondary raw material being an ash from the incineration of sewage sludge and/or animal droppings and/or animal meal and/or animal residues and/or animal bodies and/or liquid manure and/or fermentation residues, in the suspension, during a reaction between the ash comprising at least one phosphate-containing secondary raw material and the mineral acid, the hardly soluble phosphates of the ash comprising at least one phosphate-containing secondary raw material are at least partially dissolved and/or at least partially converted into a water- and/or neutral ammonium citrate-soluble phosphate phase and this suspension is then fed to a granulation, wherein the granulation which takes place in a fluidisation apparatus is a spray agglomeration and/or a spray granulation and wherein the fertiliser granules are formed so that the P_2O_5 content contained in the fertiliser granules is higher than 75 % w/w neutral ammonium citrate soluble. In addition, the problem is also solved by a fertilizer granule according to patent claim 12, which can be produced by the method.

The invention and its advantages

The method according to the invention with the characterizing features of claim 1, on the other hand, has the advantage that in the method for the production of fertilizer granules, first a suspension of at least one phosphate-containing secondary raw material and at least one mineral acid is produced, then the low-solubility phosphates of the at least one phosphate-containing secondary raw material are at least partially dissolved in the suspension and/or at least partially converted into a water-soluble and/or neutral ammonium citrate-soluble phosphate phase and finally this suspension is fed to a granulation, wherein the fertilizer granules are formed so that the $P2O5$ content contained in the fertilizer granules is greater than 75% neutral ammonium citrate-soluble. The method according to the invention makes it possible to process a wide variety of phosphate-containing secondary raw materials efficiently and cost-effectively and thus make them usable as fertilizers. In order to provide a particularly cost-effective method, the method according to the invention does not include a separation stage for pollutants, in particular heavy metals. Rather, compliance with the legal limits for pollutants in the fertilizer is ensured by the targeted selection of the phosphate-containing secondary raw materials, possibly in combination with other components. In the method according to the invention, no process residues are produced and the components used are technically completely converted into fertilizer granules.

In the text, percentages (%) refer to percent by weight (w/w %) unless otherwise stated.

Secondary raw materials are the residues that arise during the processing, preparation or production of something (surplus) and are used for a new production process. Chemical residues are also referred to as waste materials. Phosphate-containing secondary raw materials comprise a phosphate content of more than 5 % (based on P_2O_5). Phosphate-containing secondary raw materials are, for example, ashes from the mono- or co-incineration of sewage sludge, animal droppings, animal meal, animal residues and carcass-es, ashes from the incineration of liquid manure and fermentation residues as individual substances or mixtures thereof.

Fertilizers are substances and mixtures of substances that are used in agriculture, forestry and horticulture to supplement the nutrient supply for cultivated plants, especially crops, with various properties, possibly combined and/or functionalized with other materials.

Fertilizer granules are fertilizers in granular form, in particular with an approximately spherical shape, a preferably sufficient inherent strength and preferably an average granule size of 1 - 10 mm.

In the method according to the invention, a suspension is produced from at least one phosphate-containing secondary raw material, at least one diluted or undiluted mineral acid and/or optionally water and/or optionally at least one further component, such as further nutrient components and/or alternative phosphate sources. The suspension thus produced is then fed to a granulation process, forming the fertilizer granules. According to the invention, the suspension production and thus the reaction of phosphate conversion between phosphate-containing secondary raw material and mineral acid are separated from the granulation process, i.e. there are two separate process stages for the liquid phase process and the granulation. The suspension, which is produced from at least one phosphate-containing secondary raw material and at least one mineral acid, can be enriched or supplemented with further components, such as secondary raw materials, alkalis, salts, urease inhibitors, ammonium stabilizers, nutrients or the like, at any time, i.e. at least until the granulation process starts, e.g. in the case of spray agglomeration also still in the spray cone of the nozzle. The additional components are added according to the possibilities known to the person skilled in the art for adding components. Due to the type of composition of the suspension, the poorly soluble phosphate compound is converted in the suspension. The fertilizer granules comprise phosphate in a readily soluble, readily plant-available form, so that more than 75 % of the total P_2O_5 content, preferably more than 85 %, particularly preferably more than 90 % is water-soluble and neutral-ammonium citrate-soluble. The neutral ammonium citrate-soluble phosphorus content (P content) is determined in accordance with Annex 2, Table 4, No. 4.2.2 DüMV and can be used as an indication of the medium-term availability of fertilizer phosphorus (fertilizer P), i.e. over the period of approximately one crop rotation. The immediately available P content of a fertilizer is described by its solubility in water (determined according to Annex 2, Table 4, No. 4.2.1 DüMV). The higher the water-soluble P content, the faster or easier the availability of the fertilizer P for the plant.

To produce the suspension, for example, the mineral acid can be placed in a reaction container (e.g. a plastic tank with agitator), water can be added if necessary and then the phosphate-containing secondary raw materials and, if necessary, the nutrient components can be added. The phosphate-containing secondary raw material(s) can also first be dispersed in water and the mineral acid can then be added in diluted or undiluted form. Other sequences of suspension production are also possible.

The production of a raw material suspension according to the invention has various procedural advantages. The reaction, which sometimes occurs spontaneously and violently when the phosphate-containing secondary raw materials and the mineral acid are brought together directly, can be handled, controlled and regulated by the method according to the invention. The suspensions according to the invention comprise a significantly higher proportion of water compared to methods in which the phosphate-containing secondary raw materials and diluted or undiluted mineral acid are mixed directly in a quasi-moist state and, if necessary, granulated. In principle, this higher proportion of water acts as a buffer. The reaction between the phosphate-containing secondary raw material and the mineral acid, in particular for converting or dissolving the poorly soluble phosphates, takes place in the suspension according to the invention. As a result, the mineral acid is largely used up and the suspension produced for further use for the subsequent granulation according to the invention comprises a free acid content of less than 7 %, preferably less than 3 %, after the reaction according to the invention.

Corrosion during suspension production can be effectively prevented by selecting suitable equipment. This is technologically easy to realize. For example, containers, agitators etc. can be made of plastic, ceramic or coated with ceramic or enamel. Due to the very low proportion of free acid in the final suspension after the chemical reaction according to the invention, corrosion of plant components by the mineral acid during granulation can be effectively prevented.

The container (liquid reactor) in which the suspension is produced and/or temporarily stored can be tempered (e.g. cooled or heated) if necessary in order to control the reaction. Such a previously mentioned container can be, for example, a stirred tank reactor.

By producing a suspension according to the invention, the raw material components are significantly better homogenized. This results in a particularly homogeneous product. Moist mixtures, especially if local incrustations and hardening occur due to spontaneous and violent reactions, lead to inhomogeneities.

In the method according to the invention, there is no mandatory separation of pollutants such as heavy metals. However, separation of the pollutants is possible in the method according to the invention. This separation can be carried out by measures known to a person skilled in the art. Accordingly, the components of the suspension are selected and combined in such a way that ultimately a fertilizer granules is produced which meets the requirements of the German Fertilizer Ordinance (DüMV), in particular with regard to the pollutant load. Although this limits to a certain extent the range of variation or the quantity of components that can be used for the method according to the invention, it results in a cost-effective manufacturing method, as the separation of pollutants in particular is complex and expensive.

According to an advantageous embodiment of the method according to the invention, the at least one phosphate-containing secondary raw material is an ash, for example from the incineration of sewage sludge and/or animal excrements and/or animal meal and/or liquid manure and/or fermentation residues. The ash can originate from a mono-incineration or the joint incineration of sewage sludge or the like.

According to an additional advantageous embodiment of the method according to the invention, the at least one mineral acid is phosphoric acid, nitric acid, sulfuric acid or a mixture of at least two of the mineral acids. The mineral acids can be mixed in any combination, with the concentrations of the individual components of the mixture also being variable. Other components (additives or the like) can also be added.

In a preferred embodiment, the mineral acid used is a diluted or undiluted phosphoric acid. Compared to the use of other mineral acids, the use of phosphoric acid further increases the phosphorus content in the mixture. This increases the phosphate content in the fertilizer, which leads to a higher product quality, particularly in the production of phosphate fertilizers.

In a particularly preferred embodiment, phosphoric acid is used as the mineral acid and the composition of the suspension is selected such that the subsequent granulation results in granules with a neutral ammonium citrate-soluble content of greater than 35 %, very preferably greater than 46 % (corresponds to so-called triple superphosphate) and a water-soluble phosphate content of greater than 25 % or, very preferably, greater than 34 %. The fertilizer granules produced comprise a neutral ammonium citrate-soluble P_2O_5 content of greater than 35 % and a water-soluble P_2O_5 content of greater than 25 %. Of the total P_2O_5 content, a P_2O_5 content of more than 35 % is neutral ammonium citrate-soluble and a P_2O_5 content of more than 25 % is water-soluble. In addition, however, there may also be an insoluble P_2O_5 portion, e.g. of 10 %, so that the total P_2O_5 portion would be at least 45 % according to the previous example.

The prepared suspension may contain one or more nutrient components, which may be added before, during and/or after the preparation of the suspension. Nutrient components are to be understood as all substances which provide or supplement the nutrient supply for the cultivated plant in order to control and/or support the growth and development of the plants, for example components which contain nitrogen (N) and/or phosphorus (P) and/or potassium (K) and/or magnesium (Mg) and/or sulphur (S) and/or vital trace elements. In a preferred embodiment, at least one ammonium sulphate salt is added to the suspension, for example after sufficient reaction time between phosphate-containing secondary raw material and mineral acid.

According to an additional advantageous embodiment of the method according to the invention, at least one alkali and/or at least one salt is added to the suspension. Alkalis, basic salts, etc. can be added to the suspension produced in this way for any necessary further reduction of the free acid still present and/or for further neutralization or desired pH adjustment and/or as an additional nutrient component. For example, in a preferred embodiment, a diluted or undiluted sulphuric acid is used as the mineral acid and, after sufficient reaction between the phosphate-containing secondary raw material and sulphuric acid to at least partially dissolve and/or convert the insoluble phosphate phase, ammonia is added to the suspension produced. As a result, the fertilizer produced from this has an ammonium sulphate salt which can be used as an additional plant nutrient.

In a further preferred embodiment, the mineral acid used is diluted and/or undiluted nitric acid and/or diluted and/or undiluted sulphuric acid. Nitric acid contains nitrogen, while the sulphuric acid contains sulphur. Nitrogen and sulphur are typical nutrient components in fertilizers. The use of nitric and/or sulphuric acid is therefore particularly advantageous when compound fertilizers are to be produced and the ingredients of the acid serve as a nutrient supplier. If necessary, the binding form of nitrogen and sulphur in the reaction mixture can be changed.

According to an additional advantageous embodiment of the method according to the invention, the at least one mineral acid is a sulphuric acid and another nitrogen-containing raw material, such as ammonia or the like, is added to the suspension. For example, the ammonia can be added to the suspension produced in diluted or undiluted form.

According to an additional advantageous embodiment of the method according to the invention, at least one urease inhibitor and/or at least one ammonium stabilizer is added to the suspension. The fertilizer granules can comprise or be coated with urease inhibitors and ammonium stabilizers to improve the nitrogen fertilizer utilization and minimize the loss potential. The enzyme urease plays an important role in the nitrogen cycle of the soil, because without this enzyme nitrogen fertilization by the otherwise decomposition-resistant urea would not be possible. The process of converting urea into ammonium is called hydrolysis. Urea is broken down into ammonia and carbon dioxide. The enzyme urease required for this is omnipresent in active soil. Together with water, ammonia dissociates into ammonium and hydroxide. This reaction results in a significant increase in the pH value and is the cause of gaseous ammonia escaping into the atmosphere. The level of this nitrogen loss can be over 20 %. Urease inhibitors are chemical compounds that reduce or completely prevent the activity of the urease enzyme. Typical urease inhibitors are chemically classified as phosphoric acid diamides, phosphazenes and thiols, as well as derivatives of hydroxamic acid and urea, such as PPDA and NBTPT. Ammonium stabilizers are used to delay nitrification in the soil and are therefore also referred to as nitrification inhibitors. These act specifically on the Nitrosomonas group of bacteria, largely without manipulating other soil organisms. Ammonium is converted to nitrate in the soil via nitrite. Depending on the soil properties, moisture and temperature, this process normally takes between a few hours and a few days. The addition of nitrification inhibitors to ammonium-containing fertilizers prolongs the ammonium phase in the soil.

According to an additional advantageous embodiment of the method according to the invention, at least one defoamer and/or at least one dispersant is added during the preparation of the suspension. In a preferred embodiment, a defoamer is added to the suspension during the manufacturing process. This is particularly advantageous if a strong gas-forming reaction occurs when the individual components are combined and a type of foam is formed. For example, the defoamer can be introduced with the water or mineral acid or added together with the water or mineral acid or separately. The suspension can comprise at least one dispersant. The viscosity of the suspension can be adjusted by the dispersing agent, for example. A suitable dispersing agent can also increase the maximum possible concentration of ingredients in the suspension, for example. This is advantageous because less water has to be evaporated in the subsequent granulation process and more product is produced with the same feed quantity. This reduces production costs.

According to an additional advantageous embodiment of the method according to the invention, the composition and the reaction control are selected such that the suspension is heated to at least 50 °C by exothermic reactions. The suspension heated in this way is then fed to a granulation process, by which the fertilizer granules are produced. When the components are combined to form the suspension according to the invention, exothermic reactions can take place, in particular between the phosphate-containing secondary raw material and the mineral acid. In a particularly advantageous embodiment of the method according to the invention, the exothermic reaction is controlled in such a way that the suspension is heated to greater than 50 °C, particularly preferably greater than 60 °C. On the one hand, this can be controlled by selecting the type and mixing ratio of the phosphate-containing secondary raw material and/or the mineral acid, possibly in combination with an adjusted additional water content. On the other hand, components can be added to the suspension that cause or intensify an exothermic reaction in the mixture, such as free lime. It is also known to a person skilled in the art that the exothermic reaction can also be controlled by the order in which the components are added, the speed at which they are added and the mixing process itself. In the preferred embodiment, the suspension heated in this way is fed directly to the granulation without intermediate cooling. As a result, the heat of reaction is at least partially utilized in the drying and granulation process.

In the method according to the invention, the suspension produced in this way is fed to a granulation process, in which the fertilizer granules are formed. The production of the suspension and thus the reaction of phosphate conversion between phosphate-containing secondary raw material and mineral acid are separated from the granulation process according to the invention. The separation of the two process steps according to the invention also has the process engineering advantage that the process parameters can be optimized and specifically adjusted for the respective process step. Although the combination of different process steps initially seems more elegant, it generally leads to significantly greater complexity and thus to more difficult process control.

All methods known to the person skilled in the art in which a granule can be produced from the suspension produced are suitable for granulation according to the invention.

According to an additional advantageous embodiment of the method according to the invention, the granulation is a spray agglomeration and/or a spray granulation. In particular, the spray agglomeration and/or spray granulation is carried out in a fluidizing apparatus such as a fluidized bed system or a spouted bed system. In a preferred embodiment, the granulation is carried out by spray agglomeration and/or spray granulation. Spray granulation combines convective drying or solidification and granulate formation in a single process step.

In this process, compact particles (the granules) are formed by spraying liquids containing solids into a fluidized bed or spouted bed using a nozzle, in particular a pressure nozzle, which is more energy-efficient than conventional nozzles, by evaporating the solvent (usually water or similar) and allowing the remaining solids to cause particle growth. This process is often referred to as granulation drying or build-up granulation. Pressure nozzles are also often referred to as single-substance nozzles and use their own energy to atomize the supplied liquid. Additional compressed air or steam are generally not required. The pressurized liquid emerges as a jet or lamella into the surrounding gas atmosphere. Depending on the nozzle type and process parameters, a wide variety of sprays and droplet sizes are produced. In spray granulation processes, a liquid containing solids is sprayed evenly onto smaller particles through spray nozzles. These smaller particles are known as granulation cores and are usually made of the same material as the solid sprayed onto the liquid phase. They are formed either directly in the process itself by internal core generation, such as spray drying or abrasion, or on the other hand by recirculation of fine particles or crushing of excessively large granules from the sieve-grinding circuit and therefore do not need to be fed in as a solid raw material.

For the production of fertilizer granules, for example, the suspension can be introduced into a fluidized bed via the nozzles of the spray system by means of this spray granulation. The fluidized bed in the process chamber is preferably made of material of the same type and is whirled up by an upward air flow. This flow not only serves to form the fluidized bed itself, but also forms the drying agent. The supplied air flow is obtained through a supply air housing into the fluidized bed system. The supply temperature of the process air is typically between 20 °C - 400 °C. The product moisture and drying speed can be varied by adjusting the drying parameters. The air volume and temperature supplied determine the granulation conditions in the fluidized bed. The supply air housing can be divided into several supply air chambers in order to be able to set a directed flow or different air volumes. The supply air housing is separated from the process chamber by the fluidized bed floor, which serves to even out the air flow across the cross-section of the apparatus and to prevent the fluidized bed mass from falling through into the supply air housing. The suspension is sprayed onto the particles contained in the fluidized bed. The liquid evaporates on their surface and the solid material of the injected suspension adheres to the particles, which leads to almost shell-like grain growth. The vaporized liquid is removed from the process chamber with the now cooled fluidizing agent via the flash chamber and the separator chamber from the fluidized bed system as exhaust air. The particles entrained by the process air from the fluidized bed, in particular the fine dust, can be separated from the air, for example in an expansion zone integrated in the fluidized bed apparatus with cross-section extensions and in an adjoining filter system, and returned to the fluidized bed and agglomerated there. This produces a low-dust or dust-free product with an adjustable grain size range. Any undersized particles can be returned to the process and any oversized particles can be ground or crushed and also returned to the process. This means that technically the entire suspension is completely converted into product. Apparatus for this preferred embodiment is known, for example, from patent specification DE 101 46 778 B4 (method and fluidized bed system for the production of compact solid particles). Alternatively, spray granulation can also be carried out in a spouted bed apparatus. In contrast to the fluidized bed, the process gas in spouted bed systems does not enter across the entire cross-section of the process chamber, but only via two or more gaps. A process gas jet is created in the center of the process chamber. Such apparatuses are known, for example, from the disclosure documents DE 10 2005 037 750 A1 and/or DE 103 22 062 A1. For this purpose, for example, the supply air required for the formation of the solid flow is fed into a circular solid flow located in the axial direction of the reaction chamber of the spouted bed apparatus via a gap located in the lower area and in the axial direction of the reaction chamber. The liquid is introduced into this solid flow at one or more points by means of one or more single and/or multi-substance nozzles. This allows the flow conditions in the spraying area to be adjusted so that the liquid can be introduced into the solids flow in a targeted and adjustable manner. The high particle loading in the core zone results in very favorable conditions for heat and mass transfer in the spraying zone or spraying area. Furthermore, the liquid is largely deposited on the particles and these are thus evenly wetted on the particle surfaces. The uniform wetting with simultaneous high solids circulation between the spraying area and the return zone(s) means that a very uniform liquid film is formed on the material particles. The solidification process hardens the liquid and the solids remain on the particle surface. As a result, the granules grow very uniformly and homogeneously, which leads to a very narrow particle size distribution and a homogeneous particle structure.

In a preferred embodiment, the raw material components are fed via a multi-substance nozzle in such a way that a suspension produced according to the invention is fed via at least one material flow channel and at least one further raw material component is fed via at least one separate raw material channel. Multi-substance nozzles offer the possibility of very finely atomizing several liquids (such as suspensions, solutions or the like) simultaneously with one nozzle and only one atomizing medium (air, gas or steam). At the same time, intensive mixing takes place at the outlet of the nozzle orifice (example: three-substance nozzle model 0/4 S41 from Düsen-Schlick GmbH). The intensive mixing of the suspension produced and the other components can take place inside or just outside the nozzle (depending on the type of nozzle). This type of metering of the reactants is particularly advantageous if, for example, different reactants react with each other in an undesirable manner. These undesirable reactions can, for example, lead to aggregates or clumps that can block the feed lines or nozzles. Furthermore, they can, for example, lead to gelation of the suspension and thus reduce or prevent the possibility of pumping or spraying the suspension. Advantageously, the spontaneous, violent and undesirable reaction can be handled, controlled and regulated by metering the reactants in this way via multi-substance nozzles, as the reaction ratios of the reactants, for example, are easier to adjust and/or control. In addition, it is also possible to add further substances to the suspension, such as additives, nutrient components, inert substances or the like, for example, by means of multi-substance atomization. This allows the suspension to be tailored to the respective application, for example.

A particular advantage of this preferred embodiment for granulating the fertilizer granules according to the invention by means of spray agglomeration and/or spray granulation is that the granules comprise a particularly spherical granule shape. In this way, granules with a shape factor of greater than 0.8, preferably greater than 0.85 and particularly preferably greater than 0.9 can be produced. A sphericity in the range of greater than 0.90 corresponds to a very good roundness of the granules. A perfect sphere comprises a sphericity (SPHT value) of 1.

Another advantage is that the granule size and the size distribution width can be precisely adjusted. The granule size can be manipulated, for example, via the process control in a manner known to a person skilled in the art and/or via the type and composition of the suspension as well as via the choice of thermal and fluid mechanical parameters.

The shape factor within the meaning of the present invention can be precisely determined as follows using modern particle measurement techniques with digital image processing:

$$SPHT = \frac{4 \cdot \pi \cdot A}{U \cdot 2}$$

with A: Area of the projection surface of the granule;

U: The circumference of the projection area of the granule.

The sphericity (SPHT value) can be measured, for example, with a commercial measuring device Camsizer® from Retsch Technology GmbH, which is equipped with a CCD-Basic (1 pixel = 75 pm) and a CCD-Zoom camera (1 pixel = 15 pm). The mean sphericity is specified in terms of volume, the volume of the distribution being determined by the image analysis software according to generally known algorithms. The definition basis for the measured values is DIN 66141.

In order to enable very good and uniform spreading on the fields, the granules produced by the method according to the invention preferably comprise a narrow granule size distribution. A particularly narrow granule size distribution leads to the desired particularly uniform distribution of the fertilizer granules on the fields when the fertilizer granules are spread by machine. The granule size distribution is preferably in the range of 1 mm (d_{05}) to 10 mm (d_{95}), particularly preferably in the range of 2 mm (d_{05}) to 5 mm (d_{95}). The granule size distribution width can be adjusted, for example, by selecting the screen or fractionation cuts.

The fertilizer granules must comprise sufficient granule strength in order to generate as little abrasion, breakage and dust as possible during mechanical stress (e.g. transport, handling, spreading on fields). The strength of the fertilizer granules can be adjusted, for example, via the process control, preferably by selecting suitable process parameters and setting the drying speed to influence the porosity and compactness of the granules. The strength of the granules can also be manipulated. The strength can also be manipulated by the type of raw material components and their fineness. Components that act as binders can also be added to the granules. In this case, binders are preferably added which, in addition to the binding effect, also represent one or more nutrient components.

The fertilizer granules produced according to the invention can additionally receive one or more coatings if required. A coating can play an important role in maintaining the quality of fertilizers, for example by providing protection against penetrating moisture, reducing the tendency to clumping or to provide mechanical damage through handling and thus reduce dust formation. For example, any tendency to clumping during transport and storage of the fertilizer granules can be reduced with a coating containing various active ingredients, usually comprising a surface-active substance (surfactant) and a fine inert powder.

In addition, the fertilizer granules can be given a coating that controls the release of the active ingredient. Fertilizer granules coated in this way (sometimes also referred to as encapsulated fertilizer granules) are known to be effective and efficient sources of controlled release of nutrients for long-term plant nutrition. These nutrients are released slowly and in a controlled manner through the coating of the fertilizer particles, resulting in a sustained supply to the plants. Encapsulated fertilizer granules can be more effective and cause fewer environmental problems than soluble fertilizers due to their slow release of nutrients. Because the nutrients are released slowly and continuously, rather than suddenly and intermittently, the plants absorb more of them; they are therefore not leached through the soil and are not absorbed by groundwater. Such a controlled release of active ingredients can be achieved, for example, by coating them with sulphur. Such encapsulated depot fertilizers can also be achieved by polymer coatings. To produce encapsulated fertilizers of this type, for example, the polymerizate can first be dissolved in an organic solvent and then applied to the fertilizer granules. The evaporating solvent leaves behind a very uniform continuous thin polymerized layer, which forms the barrier layer of the fertilizer.

According to an additional advantageous embodiment of the method according to the invention, the fertilizer granules produced are provided with at least one coating and/or at least one functional layer, wherein the coating or the functional layer is applied during or after the production of the fertilizer granules by coating in a fluidized bed system or a spouted bed system. Numerous methods and technologies for coating granules are known to the person skilled in the art. All methods and technologies that produce a desired coating are suitable.

According to an additional advantageous embodiment of the method according to the invention, at least one coating or functional layer is applied by coating in a fluidizing apparatus (for example a fluidized bed or spouted bed system or the like) and/or drum apparatus (for example a drum coater, a rotary tube or the like).

In a preferred embodiment, the granulation and coating of the fertilizer granules produced take place in a continuous fluidized bed or spouted bed. For this purpose, the fertilizer granules are produced in the front process section by spraying and corresponding spray granulation or agglomeration. In the same fluidized bed or spouted bed system, the previously produced fertilizer granules are coated downstream of the granulation in relation to the material flow by applying a coating mixture via a separate spray system, for example. During spray granulation, the granules are built up in a shell shape as described. In this preferred embodiment, the process is thus conducted in such a way that at least the uppermost shell is formed as a coating. For this purpose, the at least one nozzle is fed with the coating mixture, which forms the last layer or layers in the continuous fluidized bed.

According to an additional advantageous embodiment of the method according to the invention, at least one additional solid is added to the granulation process. These additional components/substances can be, for example, foreign nuclei, inert substances, auxiliary substances, additives or the like. As a result, the granulation can be stabilized and/or additional components/substances can be homogeneously incorporated into the granules produced.

The method has the advantage that the suspension is produced as a spray in a granulation device from at least one phosphate-containing secondary raw material and at least one mineral acid by atomization. The term spray is used here to refer to the spray mist or spray jet generated by the at least one nozzle in the granulation device, which is produced by atomizing the individual components. The atomization of the individual components in the granulation device can be carried out by all types of nozzles, for example by means of at least one pressure nozzle, a multi-substance nozzle or the like. Different nozzles can also be used. Here, at least the at least one acid, in particular the mineral acid, and the at least one phosphate-containing secondary raw material, preferably an ash suspension, are atomized into a granulation device, e.g. a fluidizing apparatus or the like, by means of a plurality of channels, nozzles or the like. The reaction between the at least one acid and the at least one phosphate-containing secondary raw material already takes place at least partially in the spray mist or spray jet (spray). Advantageously, adding the reactants in this way makes the spontaneous and vigorous reaction manageable, controllable and controllable, since the reaction ratios of the reactants, for example, are easier to adjust and/or control. In addition, it is also possible to add further substances such as additives, nutrient components, inert substances or the like to a suspension to be sprayed, for example, by means of multi-component atomization. This allows the suspension to be sprayed to be tailored to the respective area of application, for example. In addition, by atomizing at least one acid, in particular a mineral acid, and the at least one phosphate-containing secondary raw material, in particular an ash suspension, the reaction surface is increased so that the reaction takes place at least partially in the spray jet. This makes it possible to process a wide variety of phosphate-containing secondary raw materials efficiently and cost-effectively and thus make them usable as fertilizers. In order to provide a particularly cost-effective method, the method according to the invention does not include a separation stage for pollutants, in particular heavy metals. Rather, compliance with the legal limits for pollutants in the fertilizer is ensured by the targeted selection of the phosphate-containing secondary raw materials, possibly in combination with other components. In the method according to the invention, no process residues are produced and the components used are technically completely converted into fertilizer granules.

According to an advantageous embodiment of the method according to the invention in this respect, the P_2O_5 content contained in the fertilizer granules is greater than 75 % neutral ammonium citrate soluble.

In contrast, the product according to the invention, with the characterizing features of claim 12, has the advantage that the fertilizer granules have a spherical shape factor of greater than or equal to 0.85 and a granule size distribution in the range from 1 mm (d_{05}) to 10 mm (d_{95}) and a $P2O5$ content of greater than 8 %, wherein the P_2O_5 content is greater than 75 % neutral ammonium citrate soluble. The fertilizer granules can be coated or uncoated.

The processes required for the invention, such as the granulation and/or coating process, can be carried out in batches, i.e. as a batch process, or as a continuous process.

Further advantages and advantageous embodiments of the invention can be taken from the following description and the claims.

Description of the embodiments

Two embodiments for the production of fertilizer granules are explained in more detail below.

Embodiment 1:

5 kg of sewage sludge ash (P_2O_5 = 21.3 %) is placed in a stirred container with 5 kg of water and mixed thoroughly using an agitator. To this, 12.5 kg of a 40 % phosphoric acid is gradually added over a period of 10 minutes. The mixture is then homogenized for a further 15 minutes using an agitator.

The suspension produced in this way is heated to approx. 55 °C and sprayed into the fluidized bed of a ProCell Labsystem fluidized bed system with a Vario 3 process insert from Glatt at a spray rate of approx. 3 kg/hour using a two-substance nozzle. The supply air temperature is approx. 160 °C, the exhaust air temperature approx. 90 °C and the material temperature approx. 100 °C.

To begin with, 500 g of the species' own core material with an average particle size of 0.2 mm was introduced to ensure that a fluidized bed was present from the outset. This core material was previously produced from the suspension by spray drying. When the desired average granule size of approx. 4 mm was reached, spraying was stopped and the granules were removed. The following specifications were determined for the granules:

- Grain shape round, compact; shape factor = 0.89
- neutral ammonium citrate-soluble P_2O_5 content: 46.1 %
- water-soluble P_2O_5 content: 25.2 %
- Heavy metal concentration: For all relevant heavy metals, the determined concentration was below the limit values of the Fertilizer Ordinance

Embodiment 2:

5 kg of sewage sludge ash (P_2O_5 = 21.3 %) is placed in a stirred container with 10 kg of water and mixed thoroughly using an agitator. To this, 2.9 kg of 80 % sulphuric acid is gradually added over a period of 10 minutes. Subsequently, 3.1 kg of 80 % ammonia is added to the suspension while stirring. After a further 5 minutes, 1.9 kg of mono-potassium phosphate (KH_2PO_4), 0.5 kg of MgCl and 0.5 kg of KCl are also added. The mixture is then homogenized for a further 15 minutes using an agitator.

The resulting suspension is heated to approx. 50 °C and is sprayed into a fluidized bed using a two-substance nozzle as in embodiment 1.

To begin with, 500 g of the species' own core material with an average particle size of 0.2 mm was introduced to ensure that a fluidized bed was present from the outset. This core material was previously produced from the suspension by spray drying.

When the desired average granule size of approx. 4 mm was reached, spraying was stopped and the granules were removed. The following specifications were determined for the granules:

- Grain shape round, compact; form factor = 0.87
- neutral ammonium citrate soluble P_2O_5 content: 16.0 %
- N content: 16.1 %
- K_2O content: 8.0 %
- MgO content: 4.0 %
- S content: 6.3 %
- Heavy metal concentration: For all relevant heavy metals, the concentration determined was below the limit values of the Fertilizer Ordinance

All the features shown here can be essential to the invention both individually and in any combination with one another.

Patentkrav

1. Fremgangsmåde til fremstilling af gødningsgranulat, **karakteriseret ved,**
- at en suspension er fremstillet af mindst én aske, der består af mindst ét fosfatholdigt sekundært råmateriale, og mindst én mineralsyre, hvor asken, der består af det mindst én fosfatholdige sekundære råstof, er en aske fra forbrænding af spildevandsslam og/eller dyreekskrementer og/eller dyremel og/eller animalske rester og/eller dyrekroppe og/eller flydende gødning og/eller gæringsrester,
- i suspensionen, under en reaktion mellem den aske, der indeholder mindst et fosfatholdigt sekundært råmateriale, og mineralsyren, er de vanskeligt opløselige fosfater af den aske, der indeholder mindst et fosfatholdigt sekundært råmateriale, i det mindste delvist opløst og/ eller i det mindste delvist omdannet til en vand- og/eller neutral ammoniumcitratopløselig fosfatfase og
- denne suspension tilføres derefter til en granulering, hvor granuleringen, der finder sted i et fluidiseringsapparat, er en sprøjteagglomeration og/eller en sprøjtegranulering, og hvor gødningsgranulatet er dannet således, at indholdet af P_2O_5, der er indeholdt i gødningsgranulatet og er højere end 75 vægt%, kan opløses i neutral ammoniumcitrat.

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** den mindst ene mineralsyre er phosphorsyre, salpetersyre, svovlsyre eller en blanding af mindst to af mineralsyrerne.

3. Fremgangsmåde ifølge krav 1 eller 2, **kendetegnet ved, at** der til suspensionen tilsættes mindst et alkali og/eller mindst et salt.

4. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** den mindst ene mineralsyre er phosphorsyre, og det fremstillede gødningsgranulat omfatter et neutralt indhold af ammoniumcitratopløseligt P_2O_5 på mere end 35 vægt% og et vandopløseligt P_2O_5-indhold på mere end 25 vægt%.

5. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** den mindst ene mineralsyre er en svovlsyre, og en nitrogenholdig forbindelse tilsættes til suspensionen.

6. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** der til suspensionen tilsættes mindst en ureasehæmmer og/eller mindst en ammoniumstabilisator.

7. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** der under fremstillingen af suspensionen tilsættes mindst et afskumningsmiddel og/eller mindst et dispergeringsmiddel.

8. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** suspensionen opvarmes til mindst 50°C ved eksoterme reaktioner.

9. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** det fremstillede gødningsgranulat får mindst én belægning, hvor belægningen påføres under eller efter selve fremstillingen af gødningsgranulatet.

10. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** den mindst ene belægning påføres ved coating i et fluidiseringsapparat og/eller et tromleapparat.

11. Fremgangsmåde ifølge et af de foregående krav, **kendetegnet ved, at** der til granuleringsprocessen tilsættes mindst et yderligere faststof.

12. Gødningsgranulat fremstillet ved en fremgangsmåde ifølge et af kravene 1 til 11, med en sfærisk formfaktor på mere end eller lig med 0,85, med en granulatstørrelsesfordeling i området fra 1 mm d_{05} til 10 mm d_{95} og et P_2O_5-indhold på mere end 8 vægt%, hvor P_2O_5-indholdet på mere end 75 vægt% er neutralt ammoniumcitratopløseligt.