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(72) Inventeurs/Inventors:
BAUCKE, GUIDO, DE;
DIETRICH, ARMIN, DE;
DRESSEL, STEFAN, DE;
KOPF, SEBASTIAN, DE;
MEISSNER, PAUL, DE;
WALCZYK, WOLFGANG, DE;
WALDMANN, LUDGER, DE

(73) Propriétaire/Owner:
K+S AKTIENGESELLSCHAFT, DE

(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : PROCEDE DE FABRICATION D'UNE GRANULATION DE CHLORURE DE POTASSIUM AU MOYEN D'UN CARBONATE DE METAL ALCALIN ET D'HYDROGENOPHOSPHATE

(54) Title: PROCEDURE FOR THE MANUFACTURE OF POTASSIUM CHLORIDE GRANULATE USING AN ALKALI METAL CARBONATE AND A HYRDOGEN PHOSPHATE

(57) Abrégé/Abstract:
This invention relates to a process for the manufacture of potassium chloride granulate from crystalline potassium chloride raw material, whereby the potassium chloride raw material is treated in the presence of water and prior to granulation with at least one alkali metal carbonate and at least one hydrogen phosphate additive. The invention also relates to the potassium chloride granulate obtained with the process of the invention.

ABSTRACT:

This invention relates to a process for the manufacture of potassium chloride granulate from crystalline potassium chloride raw material, whereby the potassium chloride raw material is treated in the presence of water and prior to granulation with at least one alkali metal carbonate and at least one hydrogen phosphate additive. The invention also relates to the potassium chloride granulate obtained with the process of the invention.

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PROCEDURE FOR THE MANUFACTURE OF POTASSIUM CHLORIDE GRANULATE USING AN ALKALI METAL CARBONATE AND A HYDROGEN PHOSPHATE

This invention relates to a process for the manufacture of potassium chloride granulate from a crystalline potassium chloride raw material, for example from crystalline potassium chloride obtained through flotation, evaporation, crystallisation, solar evaporation or through a hot dissolution process. The invention also relates to the potassium chloride granulate made by the process.

Potassium chloride is an important constituent of agricultural fertilisers. Potassium chloride is normally extracted in underground mining through conventional mining, through solution mining or from salt water through solar evaporation. The potassium chloride obtained in these ways is then further processed to the desired application forms.

Potassium chloride is often marketed in the form of a granulate as it has advantageous handling characteristics. When compared to fine-particle crystalline potassium chloride, the granulate tends to be far less inclined towards forming blockages, is more stable during storage, less inclined to caking and can be spread more easily and evenly when being used as a fertiliser. The quality of the potassium chloride granulate and thus the price attainable on the market are dependent on both the purity and the granulate quality.

The crystalline potassium chloride raw material obtained through mining potassium chloride, normally exhibits particle sizes that are significantly below the desired granule size. To manufacture the granulate, the potassium chloride raw materials are subjected to a standard granulating process whereby the fine-particle crystalline potassium chloride particles of the raw material are agglomerated into larger particles.

Standard granulating processes for the manufacture of potassium chloride granulate are press agglomeration and aggregation agglomeration. With the aggregation agglomeration of potassium chloride, the fine-particle starting material is intensively moved with the addition of an aqueous liquid so that numerous collisions between primary particles occur and these then collect together in the form of aggregates due to the capillary forces imparted by the liquid. These aggregates can combine with one another or with other primary particles. The constant movement results in a continuous build-up of particle layers and in the compacting of the particles so that in the end a moist granulate (green granulate) of the desired size is obtained which can then be dried and hardened to become the finished granulate. With press agglomeration of potassium chloride, the fine-particle starting material is compacted through the

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application of pressure so that very high forces are applied to some of the primary particles. This results in deformation of the primary particles in the contact area, for example through plastic deformation, which significantly enhances the adhesion of the primary particles to one another. As a result of friction heat, localised sintering can also occur leading to solid bridges forming between the primary particles.

The actual agglomeration is followed, if necessary after the drying of the moist granulate, by a classification of the primary granulate yielded, whereby the primary granulate is separated into fractions of the desired particle sizes.

Potassium chloride granulate is generally mechanically unstable. The granulate particles are damaged by the influence of mechanical forces such as those that occur during handling, during storage and in particular during transport. This results in a reduction of the particle diameter of the granulate particles and thus to a reduction in the value and also to a not inconsiderable formation of fine particles. These fine particles can lead to problems with the storage and handling of the granulate as they can cause dust for example, or can lead to the granulate particles caking if there is moisture is present.

Binding agents are often used in the aforementioned granulation processes to improve the mechanical stability of the granulate. These improve the forces of adhesion between the particles and thus improve the cohesion of the particles in the granulate. Typical binding agents are gelatine, starch, molasses, lignosulphonates, chalk and clay minerals. The selection of the binding agent will generally have a critical influence on the characteristics of the granulate, in particular its mechanical strength (abrasion resistance, hardness), its hygroscopic characteristics and its tendency to create dust. However, even with the use of these types of conventional binding agents, potassium chloride granulate normally still exhibits inadequate mechanical stability and so the aforementioned problems still arise.

SU 990755 describes the process for the manufacture of potassium chloride granulate through a press agglomeration procedure whereby sodium polyphosphate is added to the potassium chloride starting material in quantities from 0.2 to 1 % by weight relative to the potassium chloride.

RU 2083536 describes a process for the manufacture of potassium chloride granulate through a press agglomeration procedure applied to potassium chloride raw material, whereby the potassium chloride dust arising due to the press agglomeration is mixed with an aqueous solution of sodium metasilicate and then added to the potassium chloride raw material for compacting.

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US 4,385,020 describes a process for the manufacture of potassium chloride granulate, whereby the potassium chloride is processed with a phosphate binding agent into potassium chloride granulate in a drum or plate granulator.

DE 10252848 describes a process for the manufacture of potassium chloride granulate, whereby the potash fertiliser raw granulate is treated with a solution containing silicate or carbonate. Kinetic energy in the form of vibration is then applied to the treated granulate. The granulate yielded by this is then coated with a water-repellent substance, such as palmitin, in order to improve its resistance to air humidity.

CA 2,465,461 describes a process for the manufacture of potassium chloride granulate through a press agglomeration procedure, whereby hexa-sodium-metaphosphate (SHMP), tetra-sodium-pyrophosphate or tri-sodium-phosphate is added to the potassium chloride as a binding agent before compacting. The SHMP is intended to bind the moisture as well as the magnesium and calcium salts contained in the potassium chloride and thus to improve the mechanical strength, in particular during transport.

However, despite the addition of these binding agents, the mechanical characteristics of the potassium chloride granulate known from the current state of the art are inadequate, in particular if the potassium chloride granulate is exposed to an atmosphere with elevated humidity over an extended period of time. In particular, the known potassium chloride granulates exhibit inadequate breaking strength or bursting strength and unsatisfactory abrasion resistance after storage at elevated humidity.

This invention is thus based on the task of preparing potassium chloride granulate with improved mechanical strength, in particular a higher breaking strength or bursting strength and satisfactory abrasion resistance values. In particular, the potassium chloride granulate should still exhibit satisfactory or good mechanical characteristics even after longer exposure to high humidity levels, for example a humidity of 70 % RH (relative humidity) or higher, or other humidity influences resulting from ventilation, i.e. the breaking strength or bursting strength should be high even at high humidity levels and the moisture uptake should be minimal.

It was surprising to find that these challenges could be resolved by treating a crystalline potassium chloride raw material with at least one alkali metal carbonate and at least one hydrogen phosphate additive, in the presence of water, for example in the form of wet-filtered fine salts, prior to granulation. The breaking strength at higher humidity levels, for example 70 % RH or higher, is significantly increased and the moisture uptake of the potassium chloride granulate reduced through the combination of at least one alkali metal carbonate and at least one hydrogen phosphate additive (also referred to as hydrogen phosphate).

Correspondingly, this invention relates to a process for manufacturing potassium chloride granulate from crystalline potassium chloride raw material, whereby the potassium chloride raw material is treated with at least one alkali metal carbonate and at least one hydrogen phosphate additive in the presence of water prior to granulation.

The potassium chloride granulate obtainable by the process of the invention is characterised by higher mechanical strength and in particular by increased breaking strength or bursting strength, in comparison to potassium chloride granulate from an untreated crystalline potassium chloride raw material and likewise in comparison to potassium chloride granulate from a potassium chloride raw material that has been treated prior to granulation with only one additive, so either with the alkali metal carbonate or with the hydrogen phosphate additive. In addition, the granulate is characterised by high abrasion resistance. The advantageous mechanical strength comes into effect particularly when the potassium chloride granulate is exposed to moisture as a result of ventilation, e.g. an atmosphere with elevated humidity, in particular a humidity level of 70% RH or higher. This is primarily surprising as the exclusive treatment with alkali metal carbonate does not lead to a significant improvement in the breaking strength or bursting strength values for ventilated granulate.

Correspondingly, this invention also relates to the potassium chloride granulate obtained by the process of the invention.

The invention also relates to the use of a combination of at least one alkali metal carbonate, at least one hydrogen phosphate additive and water to increase the breaking strength / bursting strength and reduce the moisture uptake of the potassium chloride granulate.

This invention also relates to the use of a combination of at least one alkali metal carbonate, at least one hydrogen phosphate additive and water to increase the breaking strength / bursting strength of potassium chloride granulate that is exposed to higher humidity levels, in particular a humidity level equal to or greater than 70% RH.

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In the process of the invention, a crystalline potassium chloride raw material is used as the starting material. This crystalline potassium chloride raw material is in the following also referred to as fine salt. The crystalline potassium chloride raw material comprises primarily potassium chloride, i.e. generally at least 90% by weight, often at least 95% by weight, in particular at least 98% by weight and especially at least 99% by weight or at least 99.5% by weight, relative to the solid constituents of the potassium chloride raw material. The potassium content of the crystalline potassium chloride raw material, calculated as K_2O, normally is at least 56.9% by weight, often at least 60.0% by weight, in particular at least 61.9% by weight and especially at least 62.5% by weight, relative to the solid constituents of the potassium chloride raw material.

Depending on its origin, the potassium chloride raw material contains the related typical contaminants, in particular sodium salts and alkaline earth metal salts, primarily magnesium salts and/or calcium salts. It can be assumed that these contaminants, in particular the magnesium and calcium salts, lead to the granulate stability problems observed, in particular if the granulate is subjected to elevated humidity levels. Often the potassium chloride raw material contains alkaline earth metal salts, e.g. magnesium salts and/or calcium salts, in a total amount of 0.01 to 1.0% by weight and in particular 0.05 to 0.7% by weight, especially calculated as alkaline earth metal chloride, e.g. as $MgCl_2$ or $CaCl_2$, and relative to the potassium chloride (KCl) contained in the raw material.

The potassium chloride raw material used in the manufacturing of the granulate is normally crystalline potassium chloride obtained through mining or through solar evaporation or solution mining, which has been prepared for example through flotation, evaporation, crystallisation and/or through a hot dissolution process or through a combination of these methods. In the process of the invention, the potassium chloride raw material can also be mixed with further potassium chloride. For example, this could be material returned from the classification of the potassium chloride granulate yielded by the process of the invention, which may be comminuted. In this mix of potassium chloride raw material and additional potassium chloride, the proportion of additional potassium chloride, e.g. the returned material, generally lies in the range of 1 to 70% by weight relative to the total mass of the quantity to be granulated.

Instead of a freshly prepared fine salt, it is also possible to use pre-prepared fine salt for the granulating. For example, a finished fine salt with a potassium content of at least 60% by weight, relative to the dry ingredients and calculated as K_2O.

In general, the potassium chloride raw material is present in the form of fine crystalline salt particles. Alongside the crystalline particles, the potassium chloride raw material can also contain larger particles, e.g. from the returned materials. Normally, a potassium

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chloride raw material is used where at least 90% by weight of the particles of the potassium chloride raw material exhibit a particle size of max. 2 mm. In particular, 90% by weight of the particles of the potassium chloride raw material exhibit a particle size in the range 0.01 to 2 mm.

In accordance with this invention, the potassium chloride raw material is treated prior to granulation and in the presence of water with at least one alkali metal carbonate and at least one hydrogen phosphate additive. Alkali metal carbonate and hydrogen phosphate additives will also be referred to as 'additives' hereafter.

The treatment of the potassium chloride raw material with alkali metal carbonate and hydrogen phosphate additives can be carried out simultaneously or sequentially. With simultaneous introduction, the alkali metal carbonate and the hydrogen phosphate additives can be added separately or as a pre-mix.

Examples for suitable alkali metal carbonates are sodium carbonate and potassium carbonate, which can be introduced in anhydrous form or in the form of hydrates. In particular, the alkali metal carbonate is selected from anhydrous sodium carbonate (Na_2CO_3), sodium carbonate monohydrate ($Na_2CO_3 * H_2O$), sodium carbonate decahydrate ($Na_2CO_3 * 10\ H_2O$) and mixes of these. Anhydrous sodium carbonate is a particularly preferred alkali metal carbonate.

Suitable hydrogen phosphate additives are those with the formula $M_{3-k}H_kPO_4$, where k stands for 1 or 2 and M for an alkali metal cation, in particular Na or K, as well as their hydrates. Sodium compounds sodium dihydrogen phosphate (NaH_2PO_4) and disodium dihydrogen phosphate (Na_2HPO_4) and their hydrates are preferred, for example, anhydrous sodium dihydrogen phosphate, sodium dihydrogen phosphate monohydrate, sodium dihydrogen phosphate dihydrate, anhydrous disodium hydrogen phosphate, disodium hydrogen phosphate dihydrate, disodium hydrogen phosphate heptahydrate, and disodium hydrogen phosphate dodecahydrate, as well as mixtures thereof. Disodium hydrogen phosphate and particularly anhydrous disodium hydrogen phosphate are particularly preferred hydrogen phosphate additives. It is also possible to use hydrogen phosphate additives, in which sodium ions are partially or completely replaced with potassium, instead of the aforementioned sodium compounds.

In the process of the invention, a quantity of at least 0.05 % by weight, and in particular cases a quantity of at least 0.1% by weight, of alkali metal carbonate is preferably used relative to the solid portion of the potassium chloride raw material. The quantity of alkali metal carbonate required to achieve the desired effect does not generally exceed 1% by weight and especially 0.7% by weight, relative to the solid portion of the potassium chloride raw material. In particular cases, a quantity of 0.05% to 1% by weight, and especially a quantity of 0.1% to 0.7% by weight, of alkali metal carbonate relative to the solid portion of the potassium chloride raw material is used. In particular, the quantity of alkali metal carbonate used is governed by the alkaline earth metal salts contained in the potassium chloride raw material. Ideally, at least one alkali metal carbonate is used, in a quantity of 0.5 to 2 mole, and in particular cases a quantity of 0.8 to 1.5 mole per mole of alkaline earth metal ions in the potassium chloride raw material.

In the process of the invention, a quantity of at least 0.025 % by weight, and in particular a quantity of at least 0.05% by weight, of hydrogen phosphate additive is preferably used relative to the solid portion of the potassium chloride raw material. The quantity of hydrogen phosphate additive required to achieve the desired effect does not generally exceed 2% by weight, in particular 1.5% by weight and especially 1% by weight, relative to the solid portion of the potassium chloride raw material. Often the hydrogen phosphate additive is used in a quantity from 0.025% to 2% by weight, in particular in a quantity from 0.05% to 1.0% by weight and especially in a quantity from 0.07 to 0.4% by weight, relative to the solid portion of the potassium chloride raw material. In particular, the quantity of hydrogen phosphate additive used is governed by the alkaline earth metal salts contained in the potassium chloride raw material. Ideally, at least one hydrogen phosphate additive is used, in a quantity of 0.1 to 1 mole, and in particular a quantity of 0.3 to 0.7 mole per mole of alkaline earth metal ions in the potassium chloride raw material.

It is important that the treatment of the potassium chloride raw material with the alkali metal carbonate and the hydrogen phosphate additive is carried out in the presence of water. In doing so, the water can be from the preparation of the potassium chloride raw material, for example the water adhering to the potassium chloride particles or the water locked in by them, or the crystallisation water, and/or water which has been added to the potassium chloride raw material before or during the addition of alkali metal carbonate or hydrogen phosphate additive. The total water content in the potassium chloride raw material during the treatment with the alkali metal carbonate and the hydrogen phosphate additive typically is at least 2% by weight and especially at least 3% by weight, e.g. in the range of 2 to 15% by weight, and in particular in the range from 4 to 9% by weight, in each case relative to the solid portion of the potassium chloride raw material. Insofar as the total water content in the potassium chloride raw material before treatment with the alkali metal carbonate and the hydrogen phosphate additive is less than 2% by weight relative to the solid portion of the potassium chloride raw material, this is increased by the addition of water before or during the treatment to a value of at least 2% by weight relative to the solid portion of the potassium chloride raw material.

Often a moist potassium chloride raw material which already has the desired water content, is used. If necessary, the water content of the potassium chloride raw material can be adjusted to these values before or during the treatment with the alkali metal carbonate and the hydrogen phosphate additive.

During treatment of the potassium chloride raw material, the at least one alkali metal carbonate and the at least one hydrogen phosphate additive can be added to the potassium chloride raw material simultaneously or sequentially. In doing so it is fundamentally irrelevant whether the alkali metal carbonate is added to the potassium chloride raw material first and then the hydrogen phosphate additive, or whether the reverse order is applied or whether the alkali metal carbonate and the hydrogen phosphate additive are added to the potassium chloride raw material simultaneously. It is important that the addition of alkali metal carbonate and hydrogen phosphate additive is carried out before the granulation and in the presence of a sufficient quantity of water. Insofar as the potassium chloride raw material is dried before the granulation, alkali metal carbonate and hydrogen phosphate additives and water (if applicable) are typically added to the potassium chloride raw material before drying.

Often the alkali metal carbonate additive and the hydrogen phosphate additive are added to the moist potassium chloride raw material and then the treated potassium chloride raw material (i.e. the treated moist fine salt) is dried before granulation, in particular if the granulation is carried out by means of press granulation. In particular, the drying is carried out down to a water content of at most 1% by weight, relative to the solid portion of the potassium chloride raw material treated in this way. Then the granulation is carried out. The treated and dried potassium chloride raw material can also be stored before granulation.

For treating the potassium chloride raw material with at least one alkali metal carbonate, the alkali metal carbonate used generally takes the form of a powder and/or an aqueous solution. Insofar as the alkali metal carbonate takes the form of a powder, the particle size of the powder will not generally exceed 1 mm and in particular 0.5 mm. If the total water content of the potassium chloride raw material is insufficient, the alkali metal carbonate can likewise be added as a solution.

For treating the potassium chloride raw material with at least one hydrogen phosphate additive, the hydrogen phosphate additive used generally takes the form of a powder and/or an aqueous solution. Insofar as the hydrogen phosphate additive takes the form of a powder, the particle size of the powder will not generally exceed 1 mm and in

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particular 0.5 mm. If the total water content of the potassium chloride raw material is insufficient, the hydrogen phosphate additive can likewise be added as a solution.

For treating the potassium chloride raw material with the alkali metal carbonate and the hydrogen phosphate additive, the alkali metal carbonate or the hydrogen phosphate additive are normally mixed with the potassium chloride raw material in the desired quantities. As stated before, this mixing must be carried out before the granulation. In doing so, the total water content in the moist potassium chloride raw material during the addition of the alkali metal carbonate and hydrogen phosphate additives should generally lie in the range of 2 to 15% by weight and especially in the range from 4 to 9% by weight, in each case relative to the solid portion of the potassium chloride raw material, or should be adjusted to these values. In particular, the alkali metal carbonate is added to the moist potassium chloride raw material (i.e. the moist fine salt) before the drying. In a special embodiment of the process of the invention, both the alkali metal carbonate and the hydrogen phosphate additive are added to the moist potassium chloride raw material (i.e. the moist fine salt) in the desired quantities before the drying.

Furthermore, the process of the invention can also be used to create potassium chloride granulate that contains additional micro-nutrients such as B, Mn, Mo, Cu, Zn and Fe or mixtures of these. The micro-nutrients can be added before, during or after the granulation. For example, a potassium chloride raw material that already contains the desired quantity of micro-nutrients can be used. However, the micro-nutrients are often added during the process of the invention, e.g. during the introduction of the additives or afterwards, and the resultant potassium chloride raw material is then granulated. The micro-nutrients can also be added to the finished granulate, for example by spraying an aqueous solution of the micro-nutrients onto the granulate. The quantity of micro-nutrients does not generally exceed 1% by weight relative to the dry potassium chloride granulate and in each case is calculated as an element. For example, the potassium chloride granulate yielded by the process of the invention can contain 0.001 to 1% boron by weight.

The actual implementation of the granulation can be carried on the basis of the agglomeration processes known from the current state of the technology, as described in Wolfgang Pietsch, Agglomeration Processes, Wiley – VCH, 1st. edition, 2002 as well as in G. Heinze, Handbuch der Agglomerationstechnik, Wiley – VCH, 2000 as well as in Perry’s Chemical Engineers' Handbook, 7th. edition, McGraw-Hill, 1997, for example.

In general, the granulation is carried out as press agglomeration or aggregation agglomeration.

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During granulation by means of aggregation agglomeration, the treated potassium chloride raw material, which contains the alkali metal carbonate additive and the hydrogen phosphate additive in the desired quantities, is set in motion through the application of mechanical forces and may be treated with water or aqueous solutions of alkali metal carbonate and hydrogen phosphate additive during the granulation process. In doing so, the aggregation agglomeration can occur in a known manner as roll agglomeration, mix agglomeration or fluid-bed agglomeration, in particular as roll agglomeration. With roll agglomeration, the potassium chloride raw material, which may already contain the hydrogen phosphate additive and alkali metal carbonate constituents, is poured into a vessel with tilted turning axis and circular cross-section, preferably into a granulating drum or onto a granulating plate. The particles of the fine salt are set in motion by rotation of the vessel about the axis. The treatment with water or with the aqueous solution of hydrogen phosphate additive and alkali metal carbonate may be carried out, for example, by spraying onto the potassium chloride raw material is in motion. In doing so, a comparatively uniformly round granulate is obtained, which can be directly fed to a classification system.

Ideally, the granulation encompasses a press agglomeration of the treated potassium chloride raw material and a comminution of the material obtained from the press agglomeration. With the press agglomeration, the treated potassium chloride raw material is compacted by the application of pressure. All types of presses used for similar purposes, for example stamping presses, extrusion presses, piercing presses and roller presses, are fundamentally suitable for the compacting process.

Ideally, the compacting would be implemented by using a roller press. With roller presses, the compacting is implemented in the gap between two counter-rotating rollers. The roller surfaces can be smooth, profiled, e.g. ribbed, corrugated or goffered, or furnished with shaped pockets. Any type of surface profiling is primarily intended to improve the draw-in behaviour in the roller gap. Roller presses with smooth or profiled roller surfaces are often used. In this case, the primary agglomeration product is a ribbon-like strand that emerges from the roller gap, which is also known as slugs (or 'flakes').

The pressing forces required for the compacting, which are normally given in relation to the roller width and are stipulated as linear forces, generally lie in the range from 1 to 75 kN/cm, in particular in the range from 40 to 70 kN/cm and relate to a diameter of 1000 mm and a medium slug thickness of 10 mm. In general, the roller press is operated with a peripheral roller speed in the range of 0.2 to 1.6 m/s. Normally, the compacting is implemented at temperatures in the range of 80 to 100 °C or at the temperature that arises due to the application of the mechanical forces to the treated potassium chloride

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raw material (i.e. the treated fine salt). The material supplied for granulation may have to be heated to the temperature desired for granulation or it may still have residual heat e.g. from the drying process.

The press agglomeration may be carried out in multiple stages.

The press agglomeration of the treated potassium chloride raw material with a roller press, generally yields slugs which are subjected to comminution in order to adjust the particle size of the resultant granulate. The comminution of the slugs can be implemented using known methods, for example through milling in suitable devices, for example in impact crushers, impact mills or roller breakers.

In general, the actual granulation process is followed by a classification of the granulate. In doing so, the granulate is separated into granulate that has a particle size compliant with the specification, smaller granulates (fine portion) and possibly coarser granulate (coarse portion). In accordance with specifications, at least 90% by weight of the potassium chloride granulate used has a particle size or a particle diameter in the range from 0.5 to 8 mm and in particular cases from 2 to 4 mm. The classification can then be implemented in accordance with conventional processes, in particular by sieving.

The granulate material arising from the classification process that does not comply with the specification is generally fed back into the process.

In a preferred form of the process of the invention, a moist potassium chloride raw material, which generally contains 2 to 15% by weight and especially 4 to 9% by weight, relative to the solid portion of the potassium chloride raw material, is mixed with at least one alkali metal carbonate, in particular with anhydrous sodium carbonate and at least one hydrogen phosphate additive, in particular with disodium hydrogen phosphate, respectively in the desired quantity, resulting in a treated (conditioned) moist potassium chloride raw material. In doing so, alkali metal carbonate and disodium hydrogen phosphate can be used in the form of solids or in the form of aqueous solutions. The obtained conditioned potassium chloride raw material is then dried. The dry, conditioned potassium chloride raw material is fed, optionally with the returned material, into a press agglomeration, in particular a press agglomeration using a roller press with smooth or profiled rollers. The thereby obtained granulate or slugs are then comminuted and classified. The fine goods arising from the classification are fed to the press agglomeration system together with the dried, conditioned potassium chloride raw material.

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The granulate yielded by this can be finished using known processes, e.g. packaged and transported.

The potassium chloride granulate yielded by the process of the invention naturally contains the alkali metal carbonate additive and the hydrogen phosphate additive (or their transformation products) in the quantities used in the process of the invention, alongside potassium chloride. In particular, the potassium chloride granulate yielded by the process of the invention with at least 90% by weight, in particular at least 95% by weight and especially at least 98% by weight, relative to the anhydrous granulate, comprises:

i) Potassium chloride
ii) The additive alkali metal carbonate and/or its reaction products such as $MgCO_3$ or $CaCO_3$, in a quantity of 0.05 to 1% by weight, in particular in a quantity of 0.1 to 0.7% by weight, relative to the potassium chloride contained within the granulate and calculated as alkali metal carbonate, and
iii) The hydrogen phosphate additive or its hydrolysis/transformation products in a quantity of 0.025 to 2% by weight, in particular 0.05 to 1.5% by weight, relative to the potassium chloride and calculated as hydrogen phosphate additive.

In addition, the potassium chloride granulate yielded by the process of the invention also contains the contaminants contained within the potassium chloride raw material / fine salt, e.g. magnesium salts and/or calcium salts in the aforementioned proportions.

Furthermore, the potassium chloride granulate can also contain micro-nutrients such as B, Mn, Mo, Cu, Zn and Fe or mixtures of these. The quantity of micro-nutrients does not generally exceed 1% by weight relative to the anhydrous potassium chloride granulate and in each case is calculated as an element. For example, the potassium chloride granulate yielded by the process of the invention can contain 0.001 to 1% boron by weight.

As already mentioned, potassium chloride granulate yielded by the process of the invention is characterised by high mechanical stability even during storage in damp atmospheres, e.g. with relative humidity levels of 70% RH or higher. Also under these conditions, the potassium chloride granulate yielded by the process of the invention exhibits only minor dust behaviour and a high breaking strength / bursting strength, low moisture up-take or a high abrasion resistance.

Figure 1 shows a testing setup to determine the "breaking strength" for test samples, which includes a test stamp (1) with a cone-shaped test tip (R5) and a U-shaped test sample holder (3), in which the test sample (2) is fastened on both sides.

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Laboratory testing:

Crystallised material obtained through hot dissolution is used as potassium chloride raw material (fine material). The potassium content of the potassium chloride lies at around 60% by weight, calculated as K_2O and relative to the solid portion. The Mg content, calculated as $MgCl_2$ and the Ca content, calculated as $CaCl_2$ lies in total at around 0.13% by weight, relative to the solid portion. The grain size of the potassium chloride raw material (fine salt) generally lies at around 0.01 to 2 mm. The water content of the moist potassium chloride raw material (moist fine salt) amounts to 4 – 9% by weight, in particular 8% by weight, relative to the solid portion before drying.

In each case, a conventional powdery anhydrous sodium carbonate or disodium hydrogen phosphate with a water content of 0.01% by weight is used as an alkali metal carbonate and a hydrogen phosphate additive.

Manufacturing of test samples for the determination of the breaking strength:

3 kg of the potassium chloride of the specification cited above were mixed with the addition of 240 g of water with the respective additive in powder form for 1 min. in an intensive mixer. The moist potassium chloride raw material / additive mixture is dried for 24 h in the drying cabinet at 105 °C and is then de-agglomerated with a disc mill to a grain size of < 0.8 mm. For the "dry" comparison test, the additive is mixed in after the drying and after the de-agglomeration.

For the determination of the breaking resistance, cube-shaped test samples with dimensions of 50 x 50 x 8 mm are created from this material. The creation of the test samples (laboratory testing) is implemented by means of a hydraulic stamping press (model K50 from Komage) with a pressing force of ca. 290 kN.

Determination of the breaking strength (point load) of the test samples:

The unventilated test samples are measured immediately after being created.
For ventilation, the freshly created test samples were weighed and then ventilated as follows: The test samples were vertically fixed in sample holders and stored in an air conditioned cabinet for 72 h at 20 °C and 70 % relative humidity.

Immediately after the samples were taken out of the air conditioned cabinet, the ventilated test samples were weighed anew to determine the water/moisture uptake and were then immediately subjected to the breaking strength test.

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The determination of the breaking strength is implemented via a point load based on ASTM D5731:2008 (point load strength index). To do so the cube-shaped test sample (2) is fastened into the U-shaped sample holder (3) of the test device schematically illustrated in Figure 1, such that the test tip (R5) is aligned with the centre of the test sample (2). Then the test tip is pressed against the test sample with a speed of 1 mm/min and the force exerted on the test sample is measured with a pressure measurement device. The value of the maximum load applied to the test sample immediately prior to breaking of the test sample is determined, which is identified by the force dropping to zero. The test tip is cone-shaped with a cone angle of 60°. The tip has a radius of 5 mm (see fig. 1).

Respectively, 10 test samples (ventilated/unventilated) were used for the measurement. The values cited in table 1 for the breaking strength (point loads) are average values from 10 measurements.

Table 1: Breaking strength of test samples made from potassium chloride raw material and the additives anhydrous sodium carbonate and anhydrous disodium hydrogen phosphate or anhydrous sodium dihydrogen phosphate, laboratory testing (cube-shaped test sample):

#	Additives	Point loads - unventilated	Point loads - ventilated**	Moisture uptake at 70% RH **
1*	0.16 % by weight A11 + 0.28 % by weight P954	0.37 kN	0.32 kN	0.08 %
2*	0.16 % by weight A11 + 0.14 % by weight P954	0.36 kN	0.26 kN	0.13 %
3*	0.16 % by weight A11 + 0.07 % by weight P954	0.35 kN	0.23 kN	0.26 %
4*	0.16 % by weight A11 + 0.04 % by weight P954	0.34 KN	0.21 kN	0.23 %
V5*	0.28 % by weight P954	0.37 kN	0.28 kN	0.24 %
V6*	0.14 % by weight P954	0.33 kN	0.22 kN	0.49 %
V7*	0.07 % by weight P954	0.30 kN	0.21 kN	0.63 %
V8*	0.04 % by weight P954	0.33 kN	0.20 kN	0.72 %
V9	0.28 % by weight P954 dry	0.32 kN	0.20 kN	0.25 %

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#	Additives	Point loads - unventilated	Point loads - ventilated**	Moisture uptake at 70% RH **
V10*	0.13 % by weight A11	0.33 kN	0.19 kN	0.41 %
V11	0.16 % by weight A11 (dry)	0.33 kN	0.15 kN	0.68 %
V12	0.16 % by weight A11 (dry) + 0.28 % by weight P954 (dry)	0.34 kN	0.19 kN	0.24 %
V13*	KCl raw material without additives	0.34 kN	0.17 kN	0.63 %
14*	0.08 % by weight A11 + 0.28 % by weight P954	0.35 kN	0.31 kN	0.13 %
15*	0.32 % by weight A11 + 0.24 % by weight P951	0.38 kN	0.32 kN	0.11 %

* respectively with 8 weight % water;
** Ventilated 72 h, 20 °C, 70 % RH;
# = Test number;
V = Comparison test;
A11 = Anhydrous sodium carbonate;
P954 = Anhydrous disodium hydrogen phosphate;
P951 = Anhydrous sodium dihydrogen phosphate
60 grade MOP fine = Fine potassium chloride salt with a potassium content of min. 60.0 % K_2O.

Factory operation testing:

For testing the manufacture of potassium chloride granulate during factory operation, moist potassium chloride raw material (i.e. moist fine salt) with a residual moisture content of 2 –15% by weight, was fed to the drier, via a mixer if required. The additives stipulated by the process of the invention were then added, for example in the integrated mixer, and the mixture homogenised. The treated fine salt was then fed to the drier and thereafter passed, possibly together with the press return material, on to the presses in the granulation system. Classification/comminution yielded the finished grain, the marketable potassium chloride granulate. Insofar as this granulate has a potassium chloride content of at least 60.0 % K_2O, this is generally known as conventional
"60 grade MOP grain",.

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In production, several roller presses with return material circuits are used for the press agglomeration. The individual roller presses were constructed as follows: two counter-rotating rollers had a wafer profile on the roller surface (typical roller diameter 1000 mm, typical working width 1000 mm, gap width typically ca. 15 mm). The presses were operated with a linear force of around 60 kN/cm and a roller speed of 18 rpm. The feed of the fine salt was generally implemented by means of a central chain conveyor and a stuffing screw arranged above the presses.

The slugs accrued in the roller press were comminuted by means of an impact crusher. Then the material was classified with a conventional sieving device. The fraction with grain size 2 – 4 mm (product) was separated, the fraction with grain size < 2 mm was fed back for re-processing (fine goods) and the portion with grain size > 4 mm (coarse goods) was milled and then sieved anew.

A test fraction (test granulate) with a grain size of 2.5 – 3.15 mm was sieved out to determine the burst strength of the granulate.

The unventilated test granulate was measured at the same time as the ventilated granulate.

For ventilation, approx. 9 g of the test granulate manufactured was placed in a petri dish and weighed. For conditioning, the petri dish was stored in an air conditioned cabinet for 24 h at 20 °C and 70, 72, 73 or 74 % relative humidity. Immediately after the petri dish was removed from the air conditioned cabinet, the petri dish with the test granulate was weighed anew to determine the water uptake and then immediately subjected to the burst strength test using the following method.

The average burst strength was calculated on the basis of measurements on 56 individual agglomerates of differing particle size (fraction 2.5 – 3.15 mm) taken with the help of a tablet hardness tester of the type TBH 425D from ERWEKA. The force required to crush the granulate between the stamp and the plate of the breaking strength tester was calculated. Granulate particles with a burst strength > 400 N and those with a burst strength < 4 N were not taken into account for calculation of the average.

Potassium chloride raw material with the following specification was used for the factory operation test in table 2: KCl content around 61 % K_2O, ca. 0.2% by weight $MgCl_2$/$CaCl_2$ content, the residual moisture of the (moist) potassium chloride raw material was generally 5.7 – 6.2% by weight. The quantity to be processed was around 90 tons per hour of potassium chloride raw material.

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Table 2: Factory operation test - potassium chloride granulate with anhydrous sodium carbonate and anhydrous disodium hydrogen phosphate from filter-moist potassium chloride (KCl) raw material* at differential ventilation (burst strength in N and moisture uptake in %)

#	Additives	Unventilated	1 d / 70 %RH	1 d / 72 %RH	1 d / 73 %RH	1 d / 74 %RH
16*	0.16 % by weight A11 + 0.08 % by weight P954	83 N	47 N 0.1 %	15 N 3.1 %	<10 N 7.0 %	
17*	0.16 % by weight A11 + 0.15 % by weight P954	73 N	46 N 0.1 %	19 N 2.4 %	17 N 4.3 %	16 N 5.2 %
V18*	0.08 % by weight P954	61 N	13 N 1.1 %	<10 N 4.4%		
V19*	0.15 % by weight P954	85 N	24 N 0.6 %	<10 N 5.1 %		
V20*	0.16 % by weight A11	85 N	37 N 0.2 %	< 10 N 3.5 %		
V21*	KCl raw material (without additives)	70 N	<10 2.1 %	<10 7.3 %	<10 12.0 %	<10 14.5 %

= Test number;
1 d / 70 % RH = 1 day storage at 70 % relative humidity
1 d / 72 % RH = 1 day storage at 72 % relative humidity
1 d / 73 % RH = 1 day storage at 73 % relative humidity
1 d / 74 % RH = 1 day storage at 74 % relative humidity
* in each case with water, approx. 6 % by weight;
A11 = Anhydrous sodium carbonate;
P954 = Anhydrous disodium hydrogen phosphate;

Table 2 shows the particular effect of the combination of anhydrous sodium carbonate with anhydrous disodium hydrogen phosphate, in comparison with the individual additives. The products from tests 16 and 17 show significantly higher burst strength – even with higher relative humidity – than the products from comparison tests V18, V19, V20 and V21. The moisture uptake after one day is 0.1% or 0.1% (70% rel. humidity) and 3.1% or 2.4% (72% rel. humidity).

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Table 3: Laboratory tests with potassium chloride granulate with the additives anhydrous sodium carbonate and anhydrous disodium hydrogen phosphate and micro-nutrients**

	Additives	Point loads - unventilated	Point loads - ventilated	Moisture uptake
22*	0.16 % by weight A11 + 0.28 % by weight P954 + 0.5 % by weight B	0.34 kN	0.42 kN	0.19%

* with water 8 % by weight;

** Comparative tests see no. 1 and V12

A11 = Anhydrous sodium carbonate;

P954 = Anhydrous disodium hydrogen phosphate,

B = Anhydrous borax, calculated as boron.

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Claims:

1. A process for the manufacture of potassium chloride granulate from a crystalline potassium chloride raw material, comprising the steps of:

   treating the potassium chloride raw material in the presence of water with at least one alkali metal carbonate and at least one hydrogen phosphate, wherein the alkali metal carbonate is present in a quantity of 0.05% to 1% by weight relative to the dry weight of the potassium chloride raw material, and wherein the hydrogen phosphate is present in a quantity of 0.025% to 2% by weight relative to the dry weight of the potassium chloride raw material, and

   subsequently subjecting the treated potassium chloride material to granulation.

2. The process according to claim 1, wherein the alkali metal carbonate is selected from the group consisting of anhydrous sodium carbonate, sodium carbonate mono-hydrate, and sodium carbonate decahydrate.

3. The process according to claim 2, wherein the alkali metal carbonate is anhydrous sodium carbonate.

4. The process according to claim 1, 2 or 3, wherein the hydrogen phosphate is an alkali metal hydrogen phosphate.

5. The process according to claim 4, where the alkali metal hydrogen phosphate is selected from the group of sodium dihydrogen phosphate, sodium di-hydrogen phosphate monohydrate, sodium dihydrogen phosphate dihydrate, disodium hydrogen phosphate, disodium hydrogen phosphate dihydrate, disodium hydrogen phosphate heptahydrate, disodium hydrogen phosphate dodecahydrate, and combinations thereof.

6. The process according to claim 5, wherein the hydrogen phosphate is disodium hydrogen phosphate.

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7. The process according to any one of claims 1 to 6, wherein the alkali metal carbonate is present in a quantity of 0.1% to 0.7% by weight relative to the dry weight of the potassium chloride raw material.

8. The process according to any one of claims 1 to 7, wherein the hydrogen phosphate is present in a quantity of 0.05% to 1.5% by weight relative to the dry weight of the potassium chloride raw material.

9. The process according to any one of claims 1 to 8, wherein during the treatment of the crystalline potassium chloride raw material with the alkali metal carbonate and the hydrogen phosphate, water is present in an amount from 2 to 15% by weight, relative to the dry weight of the potassium chloride raw material.

10. The process according to claim 9, wherein the water is present in an amount from 4 to 9% by weight.

11. The process according to any one of claims 1 to 10, wherein the alkali metal carbonate is used in the form of a powder or an aqueous solution.

12. The process according to any one of claims 1 to 11, wherein the hydrogen phosphate is used in the form of a powder or an aqueous solution.

13. The process according to any one of claims 1 to 12, wherein the potassium chloride raw material contains 0.01 to 1.0% by weight of magnesium salts, calcium salts and mixtures thereof, in each case relative to KCl, and calculated as $MgCl_2$ or $CaCl_2$.

14. The process according to claim 13, wherein the potassium chloride raw material contains 0.1 to 0.7% by weight of magnesium salts, calcium salts, and mixtures thereof, in each case relative to KCl, and calculated as $MgCl_2$ or $CaCl_2$.

15. The process according to claim 13 or 14, wherein the magnesium salts are $MgCl_2$ and the calcium salts are $CaCl_2$, wherein the weight percentage of the magnesium salts, calcium salts, and mixtures thereof, are calculated in each case relative to KCl, and calculated as

$MgCl_2$ or $CaCl_2$.

16. The process according to any one of claims 1 to 15, wherein at least 90% by weight of the potassium chloride raw material has a particle size of less than 2 mm.

17. The process according to any one of claims 1 to 16, wherein the granulation encompasses a press agglomeration of the treated potassium chloride material.

18. The process according to any one of claims 1 to 17, wherein the alkali metal carbonate is added to moist potassium chloride raw material.

19. The process according to any one of claims 1 to 18, wherein the hydrogen phosphate is added to moist potassium chloride raw material.

20. The process according to claim 18 or 19, wherein the moist potassium chloride raw material is dried after the addition of the alkali metal carbonate and the hydrogen phosphate and before the granulation.

21. The process according to any one of claims 1 to 20, wherein at least one micronutrient is added to the potassium chloride raw material before or during the granulation.

22. The process according to claim 21, wherein the micronutrient contains boron.

23. Potassium chloride granulate obtained by the process in accordance with any one of claims 1 to 22.

24. Use of the process according to any one of claims 1 to 22, to reduce moisture uptake of potassium chloride granulate.

25. Use of the process according to any one of claims 1 to 22, to increase the breaking strength or bursting strength of potassium chloride granulate that has been exposed to a humidity level of 70% RH (relative humidity) or greater.

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Figure 1: