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A Production Process for Specialty Field Fertilizers

presented by

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About the IFA Technical Committee

The IFA Technical Committee encourages the development and adoption of technology improvements that can lead to greater production efficiencies and reduced emissions, as well as better health and safety standards throughout the fertilizer industry. Our mission is to actively promote the sustainable development of efficient and responsible production, storage and transportation of all plant nutrients. The Technical Committee accomplishes these objectives through a variety of channels, including:

- Technical and policy-oriented information materials. The committee regularly conducts surveys and produces reports on key industry metrics, including the IFA Energy Efficiency and CO_2 Emissions Report, the IFA Safety Report, and the IFA Emissions Report. This work enables member companies to assess their operations over time, make comparisons with similar facilities on an established level of performance, determine the need for technology improvements and identify good industrial and management practices.
- Regular exchange of information on technology developments and industrial practices. A key role of the IFA Technical Committee is to encourage ongoing technical innovation in the fertilizer industry through the development, compilation and exchange of technical information between members, researchers, engineers, equipment suppliers and other industry associations. To this end, the committee organizes a Technical Symposium every other year to examine progress in the production technology of fertilizers. Each Symposium traditionally features the presentation of 30-40 new technical papers from member companies worldwide, providing members with information on the latest technological developments. In the intervening years, the committee holds a variety of meetings to assess current industrial practices and standards, with an eye toward identifying key developments of interest to members.
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- Education and advocacy. The IFA Technical Committee recognizes that customers, markets and regulatory environments are best served by clear and concise information on the fertilizer industry and its practices and products. Because the knowledge and expertise found within the fertilizer industry is the best source for this information, the Technical Committee endeavours to educate policymakers, standardization bodies, customers and the public on industry achievements, technological advances, voluntary initiatives and best practices. The committee also encourages universities and development centres to conduct research on fertilizer product development and production processes.

(as provided by the author for distribution in Alexandria)

A Production Process for Specialty Field Fertilizers

Abstract

Through the years, the fertilizer industry has developed different types of fertilizers that satisfy the demand for plant nutrients.

Today, higher yields associated to improved crop varieties, high rates of application of fertilizers with NPK macronutrients, and better crop management practices, have increased the need for secondary and micronutrients in crop production.

One alternative is to include the micronutrient fertilizer in a bulk-blend of macronutrient fertilizers. Segregation will concentrate the micronutrient fertilizer in certain areas of the blend resulting in uneven application in the field.

Compound fertilizers offer a better alternative than bulk blend fertilizer mixes. If small amounts of the micronutrient fertilizer can be included in each granule of the compound fertilizer, then the even application of the compound fertilizer will secure an even application of the micronutrient over the whole area of application.

A process was design in which heated prills of sodium nitrate are mixed with crushed urea, then rounded and cooled. The resulting granule contains nitrogen in the form of nitrate and ammonium. The granule formation is based in the presence of an eutectic point in the solid-liquid phase equilibrium of urea and sodium nitrate. An industrial plant was build and currently is producing granules containing 30% of urea and 70% of sodium nitrate, with physical properties that allow for its bulk handling. Also, secondary and micronutrients can be added to the granules. The industrial plant produces also NK fertilizers based on the eutectic point that also exists for the urea and potassium nitrate system.

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A PRODUCTION PROCESS FOR SPECIALTY FIELD FERTILIZERS

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Introduction

Essential elements for plant growth

A mineral element is considered to be essential to plant growth and development if the element is involved in plant metabolic functions and the plant cannot complete its life cycle without the element (Tisdale et al, 1993). Essential elements are referred to as plant nutrients. Not all essential elements are required in equal quantities by plants, and different plant species also differ in their specific nutrient requirements.

Plant nutrients nitrogen (N), phosphorus (P) and potassium (K) are required in high quantities relative to the other nutrients and are designated as macronutrients. Crop demand for the elements calcium (Ca), magnesium (Mg) and sulfur (S) is similar to that of N, P and K, however they are often referred to as secondary nutrients. The elements boron (B), zinc (Zn), cooper (Cu), iron (Fe), manganese (Mn), chlorine (Cl) and molybdenum (Mo) are required in significant smaller quantities by crops and are known as micronutrients. Micronutients are also essential for plant growth and must be available in sufficient quantities to secure high crops yield and quality.

The following is the average concentration of mineral nutrients in plant shoot dry matter (Marschner, 2002).

Macronutrients	%	Micronutrients	mg kg^{-1} (ppm)
Nitrogen	1.5	Iron	100
Potassium	1.0	Chlorine	100
Calcium	0.5	Manganese	50
Magnesium	0.2	Boron	20
Phosphorus	0.2	Zinc	20
Sulphur	0.1	Copper	6
		Molybdenum	0.1
		Nickel	0.1

Dynamics of plant nutrients in the soil

Crops grown in traditional agriculture absorb nutrients that are dissolved in the soil water. The soil water containing dissolved elements available to plants is known as the soil solution. Mineral nutrients in the soil solution are derived from the soil parent material, organic matter decomposition and from the application of commercial fertilizers. There is no direct relationship between the total quantity of a chemical element present in the soil profile and the quantity of the same element that is dissolved and available in the soil solution. Differences in chemical composition of the soil parent material are responsible for differences in the concentration of nutrients in the soil solution. Factors of soil formation like temperature, available moisture, living organisms and elapsed time play a decisive role in determining the final concentration of individual plant nutrients in the soil solution. The term soil fertility refers to the level of available plant nutrients in soils (Brady, N.C. and R.R. Weil, 1996).

Nutrients can be dissolved from soil minerals by the slightly acid soil solution. However, the nutrients in the soil solution are in a dynamic equilibrium with nutrients held in the active surfaces of soil small particles. In particular, cation nutrient elements are held by the negatively charged surfaces of clay and organic matter. Less evident but also existent are the anion nutrient elements held by positively charged soil particles. Nutrients are loss from the soil solution by plant root uptake, leaching and chemical soil reactions (Tisdale et al, 1993).

The role of fertilizers

The role of fertilizers is to restore available nutrients in the soil profile to levels that are compatible with high crop yields and quality. Through the years, the fertilizer industry has developed different types of fertilizers that satisfy today the demand for plant nutrients (Engelstad, O.P., 1985).

Higher yields associated to improved crop varieties, high rates of application of fertilizers with NPK macronutrients and better crop management practices have increased the need for secondary and micronutrients in crop production (Mortvedt, J.J., 1985). Deficiencies of Ca and Mg may develop in acid soils, whereas S deficiencies are more common in soils low in organic matter. Deficiencies of microelements B, Zn, Cu, Fe, Mn and Mo may develop in soil with high pH as well as in soils under other specific conditions (Tisdale et al, 1993).

The quantity of secondary elements supplied through fertilizers is usually less than the amount of macronutrients N, P and K. The elements Ca, Mg and S are included in some fertilizers that supply the macro elements N, P and K or can be supplied to the soil through specific fertilizer products, such as Calcium Nitrate, Magnesium Carbonate or Magnesium Sulfate (IFDC-UNIDO, 1978). However, micronutrients B, Zn, Cu, Fe, Mn and Mo are rarely present in significant quantities in fertilizers carrying primary or secondary nutrients, mainly because of the generalized use of high-analysis fertilizers. Hence, specific fertilizer carriers have been developed to supply micronutrients to growing crops (Mortvedt, J.J. and F.R. Cox, 1985).

The concentration of micronutrient in the soil solution that is beneficial to crops is smaller than the concentration of macro nutrients. The difference between a deficient and a toxic concentration in the soil solution is rather narrow, in particular for specific micronutrient, crops and soils. For example, less than 0,5 kg ha^{-1} of B represent a deficiency level for tobacco, whereas under certain conditions, more than 1,0 kg ha^{-1} of B may be close to a toxic level (Collins, W.K. and S.N. Hawks, Jr., 1993).

The narrow “window of effectiveness” associated with micronutrients create special fertilizer application problems. The relatively small rate to be applied needs to be evenly distributed over the complete area of application. This is not easy to accomplish when the micronutrient fertilizer is solely applied. One alternative is to include the micronutrient fertilizer in a bulk-blend of macronutrient fertilizers. But in this case is mandatory that the final blend be highly homogenous and be kept in that condition until it is spread in the field. Segregation will concentrate the micronutrient fertilizer in certain areas of the blend resulting in uneven application. While some areas in the field will receive less than the needed micronutrient rate, other areas may receive toxic levels of application (Hignett, T.P. and G.H. McClellan, 1985).

Compound fertilizers offer a better alternative than bulk blend fertilizer mixes. If minute fractions of the micronutrient fertilizer can be evenly attached to each granule of the compound fertilizer, then the even application of the compound fertilizer will secure an even application of the micronutrient over the whole area of application (Hignett, T.P. and G.H. McClellan, 1985).

Process Design for a Compound Fertilizer

The goal of this work was to design a process to produce granules containing ammoniac and nitric nitrogen, allowing also for incorporating small amounts of other compounds; with the purpose of satisfying specific plant nutrition needs.

A granulation and two fattening processes were evaluated to achieve this objective. Granulation is a process where small particles are gathered into larger ones by the action of a binder, and fattening of a granule is a process for layering a granule with the liquid of the same or another material (Ennis and Litster, 1997).

The binary system urea-sodium nitrate, that has an eutectic point (Figure 1), is the base of this work. The eutectic composition is the combination of components in a simple system that has the lowest melting point compared to any other ratio of the components, and in a binary system it is located at the intersection of the two solubility curves (Levin, 1956). This condition, that represents an invariant point (zero degrees of freedom), was used to design a monogranule production process. The eutectic mixture, in liquid condition, sticks the particles together acting as a binder when the system is cooled.

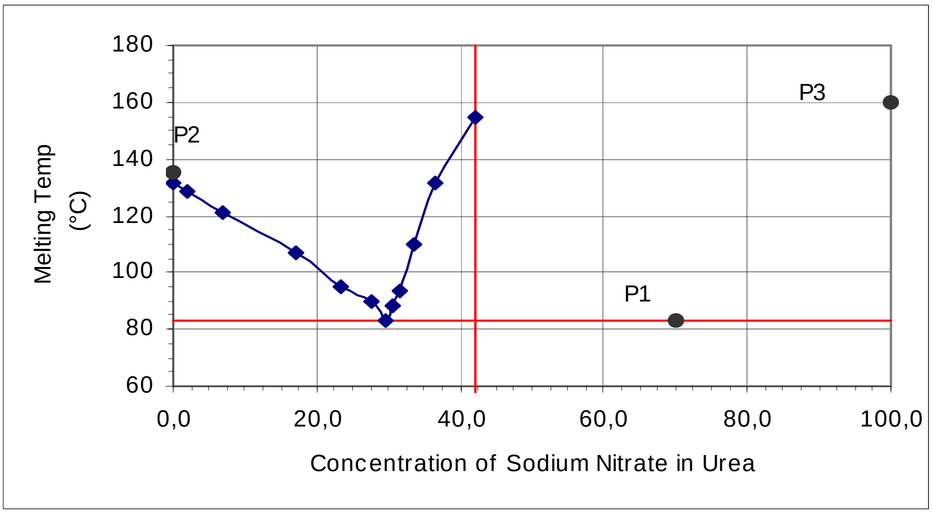

Figure 1. Phase Diagram for $NaNO_3$ – Urea

To design an industrial plant, test works were done at bench scale and pilot plants of 100 kg/h and 1000 kg/h.

The following three processes were evaluated for the process development work.

A) <u>“ Wet “ Granulation:</u>

A typical process of wet granulation for size enlargement requires a 10 to 30 % w/w of a binder solution. We used the invariant composition of the eutectic point to define the amount of eutectic mixture to be used as binder.

Considering the properties of urea and sodium nitrate, shown in Table 1 (Mavrovic et al., 1991), the energy required to produce one ton of product, using a 20% of eutectic mixture as liquid binder for the granulation, is 11,280 Kcal. This amount of energy is about 10 to 15 times lower than the necessary in a drying plant when using water as a binder. The enthalpy of the eutectic mixture measured by DTA, was 56.4 kcal/kg.

The mixture for granulation of 70% of sodium nitrate with 30% of urea, point P_1 in Figure 1, can form up to a 42% w/w of the eutectic mixture, and therefore it would have sufficient liquid for the granulation. The amount of liquid is regulated through the energy added to the system.

The advantage of this process, is that it permits to define the final size of the granule. The flow diagram for this process is shown in Figure 2. Urea and sodium nitrate prills are crushed and fed into the granulation drum where the mixture is heated at approximately 90°C to form the granules, followed by cooling, screening, and conditioning of the product.

The 100 kg/h pilot plant test showed several problems, such as, production of soft and breakable granules and clogging of the screener, specially under high humidity ambient condition. These problems could be resolved, but would result in very high operational and investment costs. Therefore, this process was left aside and no further testing was performed.

Table 1. Physical Properties for Urea and Sodium Nitrate

Compound	Melting Point (°C)	Heat of Fusion (cal/g)	Specific Heat (cal/g*°K x 10^4)	
Urea	135	60	0 °C	3.4
			50 °C	4.0
			100 °C	4.5
			150 °C	5.1
Sodium Nitrate	308	45	0 °C	2.5
			100 °C	2.9
			350 °C	4.3

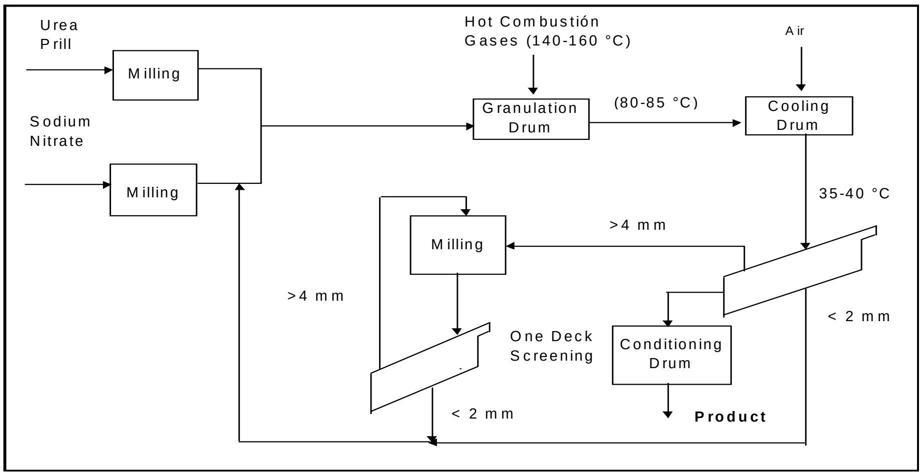

Figure 2. Flow diagram for Wet Granulation

B) Fattening of sodium nitrate with melted urea

For this process urea is melted and added onto sodium nitrate prills that are at room temperature, this corresponds to point P_2 in Figure 1.

The enthalpy for liquid urea is 60 Kcal/kg and when a 30 % of liquid urea is considered in the total mixture, there is sufficient energy to form a 65 % of eutectic mixture. Therefore it should be feasible to have in the final granule, a layer of urea on the surface, an intermediate thicker layer of eutectic mixture and a core of sodium nitrate, this is shown in Figure 3. The flow diagram of the process is shown in Figure 4. This process was tested at bench scale and the results showed that the outer urea layer was very soft and in a short time this layer became loose and detached from the granule. The expected binding phenomena was not acomplished in an efficient manner, possibly caused by the energy losses from the hot urea to the environment which competes with heating the surface of the sodium nitrate prill. This process was rejected at a bench scale level.

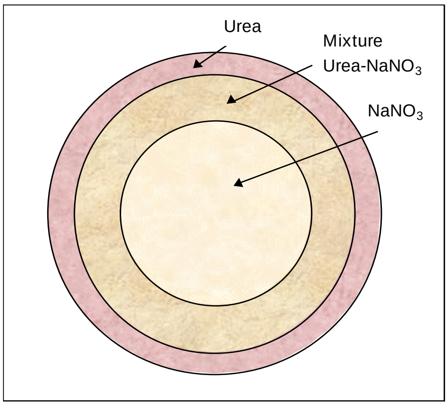

Figure 3. Final Granule

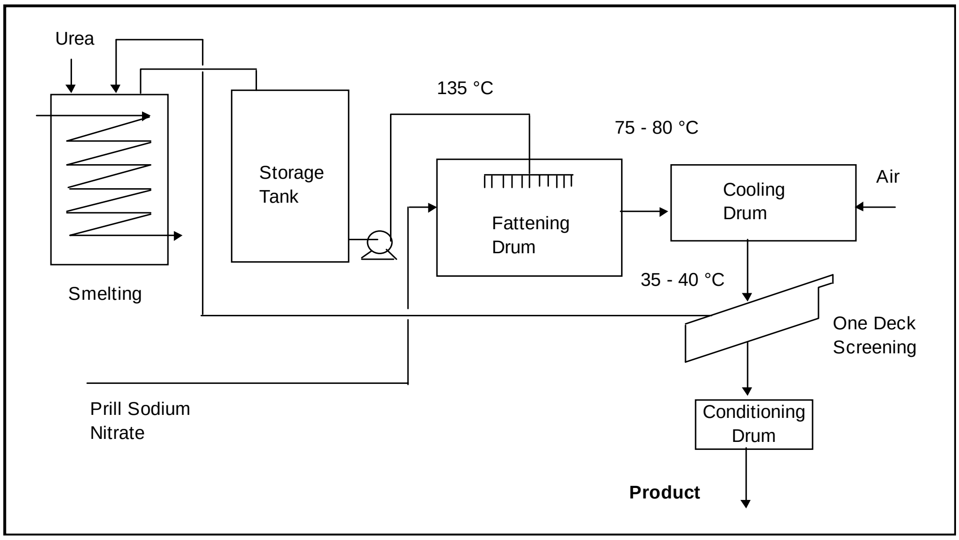

Figure 4. Flow diagram for Fattening Sodium Nitrate with Melted Urea

C) Fattening of preheated sodium nitrate with urea

When the mixture sodium nitrate-urea is heated over 160 °C, ammonia gases are produced. If a prill of sodium nitrate is heated up to 160°C, we will have sufficient energy to form 51% of eutectic mixture, and the ammonia gas formation is prevented. In this case the sodium nitrate is the energy source for the fattening process (Figure 1 point $P_{3)}$. In Figure 5, the flow diagram shows that urea is crushed and added onto the sodium nitrate prill in a pug-mixer and some of the product is recycled to the pug-mixer to reduce the temperature, avoiding that the flow becomes sticky and blocks the duct to the cooling drum. In this drum, the granules are rounded and sent to the screening deck, then to a conditioning drum, and finally cooled. This process showed excellent results in bench scale and pilot plant tests, obtaining a product with good physical properties allowing for its bulk handling. Therefore, this process was chosen for industrial application (Araya et al., 1999).

The final product is shown in Figures 6 and 7. A compound urea-sodium nitrate granule obtained from the industrial plant production, was cut in halves and evaluated with Scanning Electron Microscopy – Energy Dispersive X-Ray Analysis (SEM-EDX). In Figure 6, we can see three layers with different chemical composition, the center of the granule corresponds to sodium nitrate and over it appears the urea layer, in which we can distinguish a lighter color inner layer from the outer darker layer. The urea layer is about 400 µm and in Figure 7, we can see the result of a chemical profile analysis consistent with urea presence in the outer layer (where high carbon presence was detected).

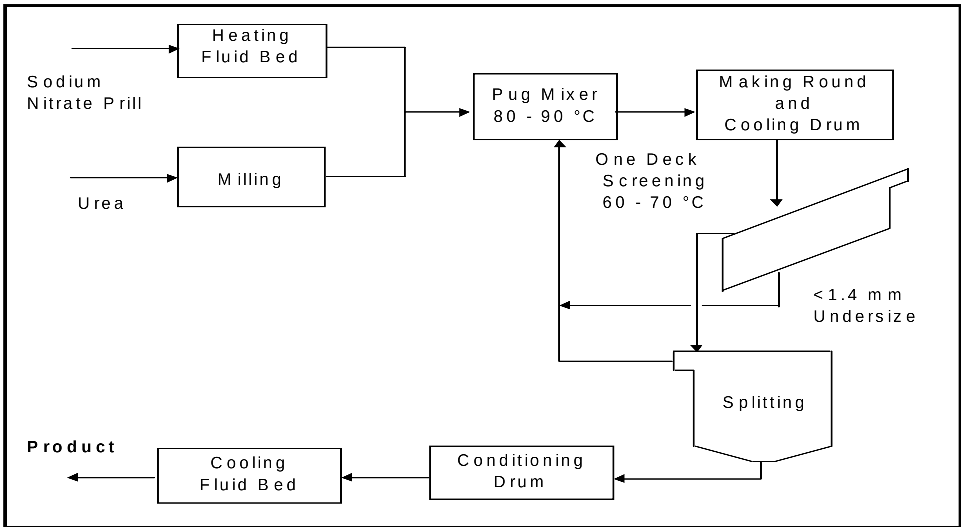

Figure 5. Flow diagram for Fattening over Hot Sodium Nitrate with cold Urea

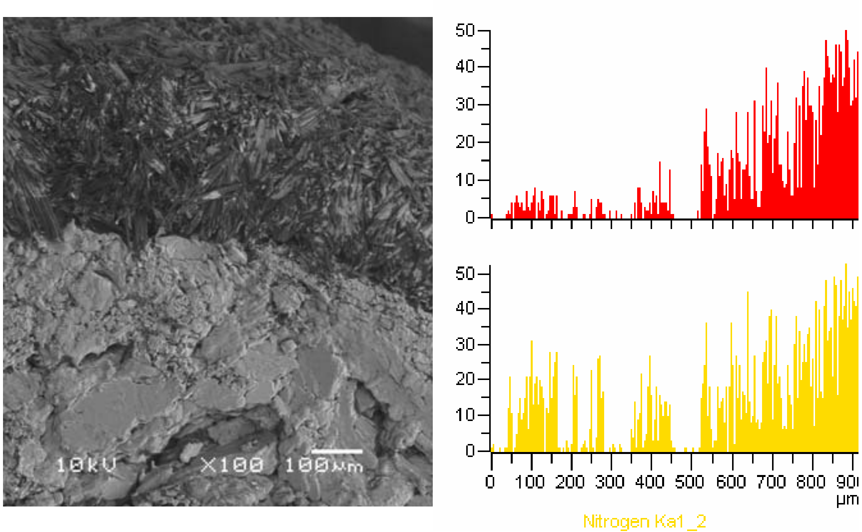

Figure 6. Backscattered electron microphotography for an urea-sodium nitrate granule. The different shades of gray relate to different chemical compositions.

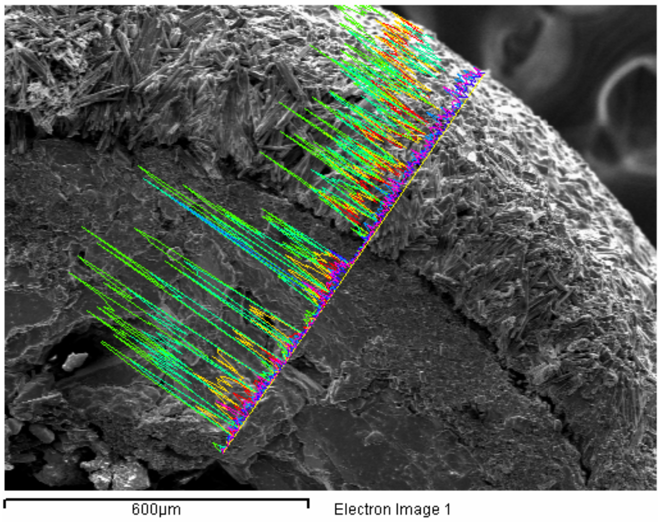

Figure 7. Chemical profile analysis made from the centre to the surface of an urea – sodium nitrate granule.

Conclusion

A process was designed and an industrial plant was built by using solid-liquid phase equilibrium information for urea and sodium nitrate. Currently, this plant is operating and producing different compound products of the type urea-sodium nitrate and urea-potassium nitrate. A variety of minor components can be added to this type of products, allowing for secondary and micronutrients incorporation into the granules, giving opportunity to design a product for satisfying specific plant nutrition needs required by the costumers. Examples of which are sodium nitrate granules with about 0.25 % of boron, and potassium nitrate granules with about 2.0 % of magnesium oxide.

Compound products with the three primary nutrients: nitrogen, phosphorous and potassium (NPK) also could be produced with the process developed in this work, combining raw materials such as urea, ammonium nitrate, monoammonium phosphate, sodium nitrate, potassium nitrate, calcium nitrate, and potassium chloride.

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