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THE GRANULATION OF SUPERPHOSPHATE AND MIXED FERTILISERS

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In recent years a large amount of information concerning the granulation of fertilizers, the results of research, has been published, much of which has become embodied in manufacturing practice. This extensive field offers so many interesting problems of a theoretical and practical nature on the course of chemical reactions and physical behaviour, as well as in technical processing, that it is not surprising if, in spite of the mass of known facts, new points of view arise which serve to deepen and complete our understanding and experience concerning the granulation of fertilizer materials. From this mass of material we shall endeavour to select some experiences concerning superphosphate and mixed fertilizer materials, set these in relationship one with another and bring what is common to all these phenomena into convenient and simple form.

A brief systematic arrangement of the granulation processes in our industry presents the following picture:

a. Natural formation as a result of rotary movement i.e., granule formation by rolling processes (rotary drum or inclined plate)

b. Forced shaping by mechanical pressure or friction (Eirich mixer, extrusion through perforated plates)

c. Processes where granulation is linked with acidulation.

These processes can be applied equally well to superphosphate and compound fertilizers.

Depending on the subsequent handling of the granules we may distinguish between:

a). Treatment followed by drying

b). Treatment without drying

Here too, superphosphate and compound fertilizers fall into both groups.

The problems arising from granulation include:

a) Chemico-physical: Reaction conditions and secondary reactions.
Reversion and other losses of nutrients;
Removal of noxious gases evolved,
Stability of the granules and caking in bulk storage,
Resistance of the packaging materials etc.

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b) Technical: Method of forming depending on the properties of the products (free acids, moisture content), degree of drying etc.

c) Economic: Drying costs, economies or reduction etc.

1. Superphosphate.

Whereas the classical type of granulating is associated with subsequent drying, whether carried out by means of oil or coal heating in various special driers or in the granulator itself by heating with steam while blowing in air, it has been shown that granules can be produced without drying, which are sufficiently hard, irrespective of the process employed. By the inclined plate as well as using mixers like the Eirich-mixer, or by pressing i.e. whether by freely formed rolling processes or by mechanical forming, superphosphate is formed into granules which harden completely and become pressure-proof after suitable curing.

Several requirements must be fulfilled:-

a) Fresh superphosphate must be used direct from the den, or at the most only a few hours after removal.

b) Its content of free phosphoric acid must be not below 5%.

c) Its moisture content must not be over 9%

This last requirement is achieved without difficulty today by fine grinding of the raw phosphate and reaction with at least 58° sulphuric acid, even in the older non-continuous type of plant. The lower the moisture content of the superphosphate, the more water may be added in the granulator in order to promote granule formation without the subsequent hardening being adversely affected, whilst a higher content of free phosphoric acid favours granule formation. Thus a superphosphate with a free P_2O_5 content of 5% and 8% H_2O, with the addition of 0 - 2% water in the granulator yields very good granules, which after eight days are ready for despatch. After a longer curing the granules harden, but the fact that the granules stick to each other in the heap is immaterial. An addition of at the most 0.5% neutralizing material to the fresh granules eases the screening, but it is not necessary for the hardening process.

When the content of free P_2O_5 is kept above 5% in the fresh material, it has not been established that this interferes with later treatment either in the granulating process or in the curing. Here we must take into account that superphosphate is handled by us on the basis of water plus citrate-soluble phosphoric acid. When sales are to be based on water-solubility, care should be taken when dusting with neutralising materials in case the free and water-soluble phosphoric acid may revert and this can upset the later reactions. According to our experience, after 4 weeks storage, a conversion rate of at least 95% is obtained, with a moisture content of 9-10% and free P_2O_5 content of 3% in the cured product. The amount of H_2O plus free P_2O_5 should not exceed 12%. Then one can be sure of hard granules and a free-flowing, absolutely stable, non-caking material

Omission of drying of course reduces the cost of the granulating process considerably. Under our conditions a saving on

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fuel oil amounting to 30 - 40% of the total granulating cost can be effected. There is also a considerable reduction in power costs. The installation will be considerably simplified and cheapened by omission of the drying drum, furnace, oil tank, cooler, plant for fume removal and transport arrangements. These savings amount to at least 50% of the total plant cost.

A particularly difficult problem is the question of acid-resistance of packaging materials. When superphosphate goes through a drying process, the action of the heat causes hydrofluoric acid to be released. This continues active for weeks, long after the product is cold, minute quantites in the form of gas attacking both jute sacks and paper sacks unless these are protected with bitumen or plastic linings, which considerably increases the price of the sacks. These delayed-action corrosives are the more severe the more the superphosphate is dried, whereas with an increased moisture content the hydrofluoric acid in cooled superphosphate is more likely to remain bound. The content of free phosphoric acid is not important, hence the demand for a minimum of free acid in the granules is unfounded unless a completely neutral product could be produced, from which no hydrofluoric acid could escape. This, however, is not possible with normal superphosphate. The difficulties of these packaging problems would be completely avoided by omitting the drying of superphosphate. The advantage is obvious. Storage in jute and paper sacks without protective linings would be possible for longer periods; this would allow early sales and distribution spread over the whole of the year and the customer would be spared the heavy costs of packing materials.

The secondary reaction of the granulated fresh superphosphate requires a certain time, which can be greatly delayed by the use of an excess of acid, and at the same time caking of the granules occurs, so that bagging and despatch of the material immediately after manufacture is not possible. Even if the necessary curing time, the length of which also depends on the type of raw phosphate, requires to be extended, this disadvantage does not outweigh the previous reduction in cost.

2. Compound Fertilizers.

All compound fertilizers which contain superphosphate can be granulated in the same granulating plant as superphosphate. The method of operation needs to be varied depending on the combination of fertilizer materials to be used, and whether they contain only phosphoric acid and potash, or nitrogen and phosphoric acid or all three nutrients.

The nitrogen, added by us partly as N-solution, alters the properties of the fertilizer considerably, the free acid is neutralised, the part of the water-soluble phosphoric acid is converted into the citrate or citric acid soluble form, and the newly introduced ammonium nitrate increases the hygroscopicity due to the potassium chloride.

Granule formation takes place easily with the potash-phosphate types with appropriate adjustment of the free acid and moisture content of the fresh superphosphate employed, either with or without very slight addition of water in the granulator. The granules attain a satisfactory hardness without drying, caking does not occur, and after 8 - 14 days curing, the product is ready for despatch. On the other hand, ammoniation makes granulation more difficult, and as well as the N-solution more water must be added, the amount depending on the proportion and properties of the components, potassium chloride and ammonium sulphate, and whether these are present in the crystalline or powdered form. When granulated first and then ammoniated afterwards, the amount of nitrogen solution is very limited, because complete penetration of the larger granules is no longer possible and an uneven distribution of the solution can be expected in consequence.

Where it is a question of manufacturing high percentage and highly ammoniated compound fertilizers (1), the heat liberated by the neutralisation of the free acids may be sufficient to cause loss of part of the water. Blowing in air in countercurrent favours this process. Hard dry granules can be obtained without the need for special drying. By blowing in steam, such concentrated fertilizers can be granulated with less water, since owing to the raising of the temperature, some of the nutrient salts are dissolved thereby facilitating granulation. The end-product contains less moisture and drying is unnecessary (2).

The marked difference in the quality of the granules produced is to be attributed to the different combinations of individual types of fertilizer. Only in favourable circumstances are the granules capable of curing and non-caking in the heap without subsequent drying. The curing of compounds made by the use of nitrogen solution will be difficult, owing to their content of ammonium nitrate. But in our fertilizers of average nutrient content, the amount of ammonium nitrate is not so great that the amount of water needed for granulation can be materially reduced while the temperature is raised in the mixture by blowing in steam, as is possible when larger amounts of ammonium nitrate are present. On the other hand it is sufficient when combined with potassium chloride to give the material a hygroscopicity, which may be very important during curing in heaps, especially in damp climates. The surface of the heap will become soft and slimy, the granules will disintegrate and this may spread through the whole heap making the product unsaleable. The same can happen with non-ammoniated fertilizers which contain a great deal of potassium chloride. Provided the goods will be bought and used quickly drying can be safely omitted. Absolute stability for an unlimited time is not yet attainable for these fertilizers, so that the omission of drying entails considerable risk as regards marketability. Therefore only in very few instances do we put undried compound fertilizers on the market. In this case the extra cost of installing and operating a drying plant is offset by the production of unobjectionable goods of unlimited stability which are acceptable to the buyer.

By the granulating and drying process the chemical reactions in the mixture are accelerated. With non-ammoniated fertilizers, the hydrochloric acid gas liberated by the action of the free acid on the potassium chloride must be precipitated after it has passed through the dust extractor. These fertilizers cause destruction of the sacks, even when they have been well cured and bagged when completely cold. The same considerations apply as with dried superphosphate, hydrofluoric and hydrochloric acids exerting a similar effect. With ammoniated fertilizers there is no packaging problem. With potash-phosphate fertilizers no reversion of the water-soluble phosphoric acid occurs, and the secondary reactions in the superphosphate will not be disturbed, so long as heating in the drum dryer is not too intense or prolonged. The moisture content should not be reduced below 2%, since below this reversion can occur. With ammoniated fertilizers the chemical conditions differ to the extent that with neutralisation of the free acid, part of the water-soluble phosphoric acid is converted into citrate or citric acid soluble form. But the proportion of monocalcium phosphate which remains constant during ammoniation is not altered so long as the temperature of the material on leaving the drum dryer does not exceed 90°C. This limiting of temperature prevents loss of ammonia gas and decomposition of ammonium phosphate and ammonium nitrate, as this will not occur below 160°C. The formation of diammonium phosphate by ammoniation is so slight, that loss of N through decomposition of this salt, which begins at a temperature of about 60°C, is practically negligible.

Whilst dried potash-phosphate fertilizers show no inclination to cake in the heaps, this characteristic is a great nuisance with some types of ammoniated fertilizers. According to recent data (3) this caking is to be attributed to the fact that during manufacture ammonium sulphate and potassium chloride react together to form ammonium chloride, which is deposited on the surface of the granules by sublimation, and causes caking by coalescence of the crystals. This is helped by high drying temperatures as well as by the presence of too great a proportion of fines and small granules resulting from insufficient screening. Caking should therefore be prevented by as low drying temperature as possible and complete fines extraction. On the other hand well dried granules tend to cake less than those with a higher moisture content, especially when the latter are put in the curing heaps while still warm. Therefore it is necessary that ammoniated fertilizers shall be dried at the lowest possible temperature to the lowest possible moisture content in order to lessen the tendency to cake. An intensive cooling of the product on leaving the drum dryer reduces caking tendencies so that it is possible in favourable cases for dried material to be bagged, as soon as it is cool enough.

The sprinkling of wetting agents over the finished granules as a means of preventing caking has also been tried. Unfortunately the hopes that were entertained of these materials have not yet been fulfilled. According to our experience no difference has so far been established as regards hardness between treated and untreated granules. This is a field in which extensive research is required before final judgement can be given.

The conditions for the individual fertilizer types are quite different and appear, quite apart from the reasons given, to depend as much on the granulating - and drying - apparatus employed, as on the degree of ammoniation and the nature of the raw material employed. These relationships have not yet been fully investigated. When it is not possible to pack the fertilizer immediately, as in the unfavourable cases described above, it is sufficient, nevertheless, to cure for a maximum of 2 weeks to allow the reaction in the heap to come to an end. After crushing the lumps, the material can then be bagged, since further caking does not occur in the sacks.

With the object of setting up the granulating process for superphosphate and mixed fertilizers on a simpler and more economic basis, various methods have been developed. These depend on the principle of combining acidulation of the superphosphate with granulation and any necessary drying, making use of the considerable quantity of heat liberated during the reaction, instead of using the finished superphosphate. It is to be hoped that such processes will prove their worth in practice, for it cannot be denied that we require bigger and bigger plants, costing more and more, in order to introduce the smallest change of form in our fertilizers. Although owing to technical developments, granulation plants have been simplified, requiring less invested capital, and the production costs considerably reduced, there remain for the superphosphate industry many problems of this kind, and the work of solving them continues.

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