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AN IMPROVED METHOD OF PRODUCTION FOR COMPLEX FERTILIZERS

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France).

For a number of years now, the PEC Company has been designing and using a set of processes and equipment for the production of complex fertilizers, on the basis of two strictly individual stages of operation. The first stage includes chemical reactions as a whole, in the liquid phase, but more or less slurry-like. The second stage includes granulating and drying the resultant slurry.

It appeared, however, that this set of techniques, although perfectly adapted to such conditions as prevailed when the methods were first adopted, did not allow a fully productive use of improvements made by the chemical industry in the meantime and which will progressively conquer the market, more particularly the production of more and more concentrated nitric and/or phosphoric acids.

Ammoniation of slurries made with such acids - whether with or without acidulation of rock-phosphate - results in pH values still far removed from the desired neutral point, and in thick slurries which cannot be sprayed - unless considerably watered down - for granulating and drying operations. This destroys the advantage of highly concentrated acids which should, theoretically, allow considerable savings on fertilizer drying costs.

This is why PEC research services have been exploring for many years a method allowing the best possible use of such acids. In 1958, it appeared to them that the less costly process involved the ammoniation of nitrophosphoric liquors as far as is permitted by the viscosity of the medium in PEC reactors, characterized by highly efficient stirring.

At that time, such more or less thick liquors were processed in either a solid or semi-solid medium by adding recycled fines, to produce wet granules. A set of patents was registered to cover both the principle of this process and the specially designed apparatus to carry it out. However, the complete ammoniation of such granules was a rather difficult and fairly inefficient process.

We therefore proposed making use of the formation of the granules in successive coatings, each coat being individually ammoniated.

To check this idea, small grains of complex fertilizers made by the conventional process were sprayed with slurry and processed by ammoniation. It was observed that ammonia was easily and readily fixed until the surface coat became neutral. A further, especially interesting observation was that, owing to both the evaporation caused by the heat from the ammoniating reaction, and the normal thickening corresponding to a higher ammoniation rate, the resulting granules had a dry aspect and the coat was sufficiently hard to allow handling the granules as necessary. On this basis, our engineers were able to develop the complete process.

In a bank of PEC reactors, a slurry is made by neutralizing the necessary acids - if necessary after reacting such acids with a given ratio of rock phosphate - by injecting gaseous ammonia until a thick slurry is obtained. During this first stage, care is taken to 'jump' any intermediate pH ranges where thickenings may occur. This is made especially easy by the 'cascade' treatment in the PEC bank of reactors.

A specially engineered unit is used to finalize neutralization, possibly together with either total or partial conversion - by adding acid simultaneously with ammonia - of any  $(NO_x)_2$  generated during acidulation in those processes which include such an operating stage. This unit is a cylindrical drum with a horizontal axis. The interior face of the cylinder is smooth, so that the material in it moves as a rolling bed. Fines recycled from previous operations are added at the inlet, to act as nuclei for granules. A preammoniated slurry is sprayed over this bed of fines, in either one or several points, according to the size of the unit. Compressed air is used with thicker slurries.

Under the combined effect of spraying and bed rolling, the particles get coated with a fine layer of slurry.

The fresh slurry thus offers a maximum surface area for easy ammonia absorption. The ammonia is introduced under the bed, at the place where the bed is thicker, so that the ammonia may have the maximum contact time with the growing granules.

Although this type of unit works according to a different principle, the idea of introducing ammonia under a rolling bed in a cylinder was already used, more generally with a manifold of drilled tubes located parallel to the cylinder axis.

However, we observed that a manifold located in this way offers a high resistance to the rotation of the cylinder, with a risk of dislocating the tubes - at least when the conditions inside the cylinder worsen - and a rapid wear of the manifold. As a consequence, the distribution of ammonia is difficult to regulate.

It was therefore decided to use a system made of forks located at right angles to the cylinder, with the arms of the

forks near the internal wall of the cylinder, moulded to the cylinder shape as soon as they enter the bed.

The fingers of the forks are hollow, coated externally with a plastic material to facilitate the passage of the granules and slotted lengthwise at their ends on both sides of each finger so that the ammonia may be delivered in horizontal gas sheets.

Each fork includes either two or three fingers and is fed with ammonia through a rotameter. Several forks are set parallel to one another according to requirements. As they are fed individually, the ammoniation of each specific area may be easily adjusted when needed.

This design proved perfectly satisfactory, with practically no lamination of grains by the jets and no clogging of injection slots.

A few examples, chosen among various processes, are given below.

#### Carbonitric process

For this process, it was only barely possible, using 65% nitric acid, to neutralize the liquor down to pH 8, but the conversion of  $(\text{NO}_3)_2 \text{Ca}$  was not feasible. Consequently, carbon dioxide had to be injected into the cylinder together with ammonia, using two sets of superimposed forks, one for carbon dioxide and the other for ammonia. To our surprise, it appeared that the reaction evolved in a peculiarly favourable way. During some tests it was even possible to fix both carbon dioxide and ammonia over and above the total calcium nitrate conversion, i.e. as ammonium bicarbonate covering the grains with a white film, with practically no ammonia smell in the gases at the cylinder outlet.

When working with concentrated acids, the granules coming out of the cylinder are perfectly spherical and sufficiently strong to be directly screened.

Under such conditions, under-size particles were directly recycled, and over-size ones were merely dried in a conventional dryer and passed through a cooler. This drying proved necessary despite the low water content of the granules obtained.

In the case of ternary fertilizers, and when the potassium content is not too high, the chloride may be usefully added to the slurry before spraying, since the latter is often fluidized in the process.

Practical operating conditions are as follows :

Phosphate rock from Morocco is treated with 65% nitric acid at a mole ratio of  $\text{N}/\text{P}_2\text{O}_5 = 6.3$ . Just before the reaction stops, a stabilizer - magnesium sulphate - is added.

Pre-ammoniation is carried out to about pH 8.

In binary tests, the resultant slurry is sprayed over the bed of fines in the drum. Both ammonia and carbon dioxide are injected in the drum head forks, and carbon dioxide only, as a finisher, in the tail fork. A flow of air heated to 400° C is directed at the top of the bed, so that the temperature in the bed is kept around 60° and the outgoing granules are core-dry.

In this way, using a pre-ammoniated slurry holding:

N as ammonia	4.47
N as nitric acid	8.0
Total P <sub>2</sub> O <sub>5</sub>	13.70 (97% soluble)
H <sub>2</sub> O	17.50

a marketable granulate was obtained with the following composition :

N as ammonia	7.95
N as nitric acid	8.35
Total P <sub>2</sub> O <sub>5</sub>	14.50 (97% soluble)
CO <sub>2</sub>	4.70
H <sub>2</sub> O	4.75
(NO <sub>3</sub> ) 2 Ca	0.80
Vapour tension	51.5%

The mesh sizes of the product at the drum outlet were :

fines	40%
marketable (mesh 12 to 7)	53%
over-size	7%

The efficiency rate was 78% for ammonia and 45% for carbon dioxide absorption. Ammonia was easily recovered from the gases by scrubbing with the acidulation liquor.

Ternary fertilizers are made by adding chloride to the slurry before it is sprayed over the bed.

Starting from a binary slurry with the following composition:

N as ammonia	3.55
N as nitric acid	7.08
Total P <sub>2</sub> O <sub>5</sub>	11.15 (96% soluble)
H <sub>2</sub> O	12.5
K <sub>2</sub> O	11.25

a marketable product was obtained, with the following composition :

N as ammonia	6.77
N as nitric acid	7.00
Total $P_2O_5$	11.1 (96% soluble)
$K_2O$	11.2
$CO_2$	4.45
$(NO_3)_2 Ca$	0.09
$H_2O$	5.2
Vapour tension	64%

The mesh sizes of the products at the outlet were :

Fines	47.5%
marketable	45.0%
over-size	2.5%

Absorption rates for both ammonia and carbon dioxide are about the same as for binary compounds.

It should be noted that calcium nitrate is practically eliminated. As a result, the balance of water vapour tension is particularly high, indicating an extremely low hygroscopicity in the fertilizer.

#### Sulphonitric process

A 1-1-0 type fertilizer was prepared, with at least 50% of its phosphoric acid in water-soluble form. This was carried out by increasing the amount of sulphuric acid, as compared with the conventional process, in order to block the calcium in the rock phosphate until free calcium amounted to only about 1 Ca for 1  $P_2O_5$ .

We know that, in such cases, a stabilizer such as Mg sulphate should be added in order to avoid any reversion of water soluble  $P_2O_5$  into citrate soluble  $P_2O_5$  through interaction between ammonium phosphate and calcium sulphate.

Rock phosphate (Morocco grade, 33.5%  $P_2O_5$ ) is reacted with 4.4 moles  $NO_3H$  (as a 52% acid) through  $P_2O_5$ .

98% sulphuric acid is added, some towards the end of the reaction, and the remainder during pre-ammoniation, up to 2.7 moles  $SO_4H_2$  per  $P_2O_5$ . Magnesium sulphate - 7% of the phosphate by weight  $\frac{4}{2}$  is added towards the end of the reaction.

Pre-ammoniation is carried on until about 40% of the total required ammonia is integrated. The slurry is sprayed over

recycled fines in the ammoniating drum, and ammoniation occurs as explained above.

Under such conditions, starting from a pre-ammoniated slurry with the following composition :

N as ammonia	2.45
N as nitric acid	4.67
Total $P_2O_5$	12.5 (100% soluble)
$H_2O$	16.0

a marketable granulate was obtained, with the following composition :

N as ammonia	6.80
N as nitric acid	4.90
Total $P_2O_5$	13.20 (97% soluble, of which 64% water soluble)
$H_2O$	6.0
pH	5.6

mesh sizes of the product at the drum outlet were :

fines	44%
marketable	43%
over-size	13%

#### Ammoniacal fertilizers

The tests were extended to the preparation of a fertilizer in which the nitrogen was purely ammoniacal, by neutralizing the ammonia with a mixture of sulphuric and phosphoric acids.

The 42% phosphoric acid is first partially neutralized, and 98% phosphoric acid is added to the following units while the injection of ammonia proceeds up to about 40% of the total required amount of ammonia.

The resulting slurry is sprayed over the bed of small granules in the drum. Simultaneously, ammonia is injected into the bed up to the required amount to maintain the pH of coated granules in the 5.2 - 5.3 range.

The temperature in the bed is maintained around  $100^{\circ}C$  (too high a rise in temperature could result in melting the product in the drum and clogging the outlets.)

The final product is a mass of hard, strong granules, with about the same mesh-size as in the previously mentioned tests.

The resulting marketable granulate shows the following composition :

N as ammonia	16.0
Total P <sub>2</sub> O <sub>5</sub>	31.1
pH	5.25
Moisture	1%

The efficiency of ammonia absorption in the drum was 92.5%.

#### Summary.

Faced with the advent of concentrated acids on the market, the PEC Company investigated how such acids could be directly used without any further dilution.

With this in mind, a sufficiently versatile process was designed, in which reactions are carried out in the liquid phase as far as viscosity permits, taking into account the high efficiency of typical PEC reaction tanks.

The resulting slurry is then sprayed over a bed of growing granules in an ammoniating drum with a smooth interior face and individually adjustable ammonia injectors.

Under such conditions, each tiny initial particle is coated with successive slurry layers which are ammoniated just as they form. These very thin layers have a very high absorption power. Moreover, such neutralizing, thanks both to the evaporation it produces and the reactions which occur at this stage, results in an immediate hardening of the coats, avoiding any clogging in the cylinder and allowing the handling of final granules without any special precautions.

Fines may be recycled immediately, and over-size, after grinding in a roll-crusher.

Only the marketable product requires some final drying, in order to eliminate the small remaining amount of water which could affect storage life.

Much less fuel is thus required than with conventional processes, and much simpler equipment may be used.

The profitability of the process will now be checked by means of full-scale tests.



DISCUSSION

Mr. Y. BERQUIN (Potasse et Engrais Chimiques, France) : As we have seen from several of the papers already presented, the present trend is towards the use of processes which have been very properly described as auto-thermal. Our company, which has always been concerned with problems relating to complex fertilisers, has also sought to develop methods enabling it to produce fertilisers at least cost, bearing in mind the current state of technological progress, whilst at the same time not departing too far from its own processes as far as their chemical aspects are concerned. The path chosen, in accordance with the present trend, was that making direct use of fairly highly concentrated acid. We have therefore presented you with a brief account of the first results obtained with our basic processes which, I would remind you, are nitro-carbonic, nitro-sulphuric and nitro-phosphoric. We have even made an incursion into the field of ammonium phosphates as such. To do this, we have attempted to develop an apparatus offering advantages over the classical types of apparatus and also giving the possibility of eliminating some of their well known disadvantages. Although the number of trials carried out is already considerable, we should bear in mind that the field covered by our research is very large and we are still in the first stage of experimentation; for these trials aimed above all to define the eventual limits of application of the new process.

These first results are, in fact, very promising, for they have revealed a good level of fixation of ammonia, enabling us to achieve a relatively high N:P<sub>2</sub>O<sub>5</sub> ratio, compared with the results generally obtained with wet processes.

Mr. N. KOLMEYER (Windmill Fertilizers, Holland) : In the past, the PEC Company has made many contributions to the development of commercial processes for the production of complex fertilisers. The traditional process of acidulating rock phosphate with nitric acid presents the producer with the problem of having to evaporate off large amounts of water in their granulating plants. Thus, their installations are characterised by the presence of large driers, whilst the equipment must have a large transportation capacity in order to meet recycle requirements. The water is either included in the acids used for the formulation or, for certain grades, added afterwards to keep the slurries manageable in the wet part of the plant. Consequently, these producers are interested in any new development which will reduce the amount of water to be evaporated or by which the problem of slurry thickening may be overcome. In this way, the capacity of existing units would be increased, whilst the fuel consumption per ton of fertiliser is reduced. The investment in new plant would be much lower.

Mr. BERQUIN has pointed out that there is a trend towards higher concentration in the manufacture of nitric and phosphoric acid. With the techniques presently available, it is possible to produce 65% nitric acid at almost the same cost price as 53% acid. This is not so far the case with phosphoric acid, since there is still no generally accepted procedure allowing straight production of high strength acid, and it is still necessary to concentrate from a filtrate strength of about 30%.

However, improvements to the steam heated vacuum evaporators frequently used for this purpose have made them much more reliable. This enables the manufacturer to make more economic use of the by-product steam from an adjacent sulphuric acid plant if it is not required for other purposes.

Even the PEC reactor battery, which is capable of handling and efficiently ammoniating very viscous and concentrated slurries, would not seem able to take full advantage of these higher acid strengths.

The principle of mixed phase ammoniation which you have been investigating is not a new technique, as others have employed this method before - either forced upon them because of less efficient reactor systems or to make use of specific advantages connected with this technique. However, a surprising and new feature of your method is that when high recycle ratios are applied - so that granulation is achieved by a coating mechanism rather than by agglomeration - granules are formed during ammoniation which are hard enough to allow direct screening and even crushing of oversize in some cases. The result is that only the marketable product requires final drying, so that we may say that full advantage has been made of the use of concentrated acids.

As a result of this development, the PEC plant should generally be able to handle even more viscous slurries than formerly.

With this in mind, I should like to ask the following question:

In many countries there is a preference for a high percentage of water soluble  $P_2O_5$  in complex fertilisers. For grades which are high in percentage plant food, the manufacturer has no other choice than to prepare ammonium phosphate, using phosphoric acid and ammonia in the process. However, for the low and medium percentage grades, leaving aside the completely different process using mono-calcium phosphate, one is left with the choice of

- a) reacting phosphoric acid with ammonia and adding a filler to make the balance; or
- b) reacting phosphate rock with sulphuric acid, resulting in a mixture of phosphoric acid and gypsum, and then ammoniating this slurry after the addition of a stabiliser to prevent reversion.

In theory it is possible to prepare, for example, a 12-12-12 fertiliser with 100% water soluble  $P_2O_5$  when partially practising the second technique. When only the raw materials are considered, the latter method is the cheapest, because the phosphoric acid is produced in situ. Moreover, it would ease demand on the phosphoric acid plant, which may also be an advantage. However, this second way of proceeding gives the most viscous slurry. It would therefore be interesting to know if such a slurry can be handled without any dilution.

In order to compare other systems with your new procedure, I should also like to ask if you know the maximum N/P ratio to which you can ammoniate the ammonium phosphate fraction.

Mr. BERQUIN : Thank you, Mr. Kolmeyer. I think you raise two questions in particular. The first relates to the preparation of formulations with a high content of water soluble  $P_2O_5$ , but in relation to fertilisers of medium analysis. The solution you propose consists in leaving in the slurry all the calcium phosphate produced during the reaction of sulphuric acid with phosphate rock. Naturally, this is one way of obtaining the desired result, but in our trials so far we have mainly tried to conserve the layout and the plant which we have hitherto been accustomed to use. A purely sulphuric attack of the phosphate rock requires a completely different apparatus to our classical apparatus. This is the reason why we have not so far explored this path - which, obviously, is not to say that it is impossible. But what we have already done - and the examples we have quoted show this - is to use a nitro-sulphuric attack which enables us to use our classical apparatus.

Although it seems to us that, as far as economic and agronomic reasons are concerned, a fertiliser containing 50% of its  $P_2O_5$  in water soluble form is very satisfactory, one can obviously go higher. To do this we have used nitric acid of up to 65% concentration, and 98% sulphuric acid. We have thus derived full benefit from concentrated acids.

Here I should just like to note that we have observed - and this is a partial reply to certain questions - that the quantity of water present in the slurries could be reduced to a surprising extent without making them impossible to handle, at least by energetic means. If in the plants which we are currently operating we are unable to derive full benefit from this low water content, it is not because of problems relating to handling but rather because of problems of crystallisation. For in certain plants currently used by us, when the water content is small, the product can be easily pumped and even sprayed, but granule formation is bad. Thus, in many cases, providing certain precautions are taken in the method of operation, one can have slurries which can be pumped and sprayed, containing very small quantities of water, e.g. about 10% with the nitro-carbonic and nitro-sulphuric processes.

You asked a question relating to the maximum level of ammoniation of phosphoric acid we can attain. Our paper, which was prepared some months ago, mentions only ammonium phosphate. As you will have seen, a molecular ratio of  $NH_3:P_2O_5$  of about 1.65 to 1.67 was possible. Since the preparation of the paper, we have continued our trials and have given particular attention to the nitro-phosphoric process. The preparation of ammonium phosphate in the presence of ammonium nitrate offers the possibility of achieving the same level of ammoniation. For example, we intended to produce an 18-18-18 fertiliser, and during trials we achieved the following results :

Total N	18.6%
of which nitrate N	6.15%
Total P <sub>2</sub> O <sub>5</sub>	18.3%
K <sub>2</sub> O	16.6%
Moisture	3.7%

I must, of course, admit that the trial was not perfect. There is a slight surplus of N and P<sub>2</sub>O<sub>5</sub> and a deficit of K<sub>2</sub>O. But if you analyse the nitrogen for nitrogen in ammonium nitrate and nitrogen in ammonium phosphate, you can observe that there again we are within the region 1.65 NH<sub>3</sub>/P<sub>2</sub>O<sub>5</sub>, i.e. 3.3 N per unit of P<sub>2</sub>O<sub>5</sub>.

With regard to the example at the end of the paper, I should also mention that the amount of water in the product emerging from the plant was, as I have just said, 3.7%; but the product was, in fact, already very hard and of a very good appearance. But since this moisture content might seem too high, we dried the granules by the classic methods down to a moisture content of 1.6%. We observed that the amount of ammoniacal N, compared to P<sub>2</sub>O<sub>5</sub>, had remained practically unchanged. In other words, we had had almost no losses, at least in the few trials which have been carried out. We suppose that this is due to the fact that the product entering the drier already has a very low residual moisture content, which probably avoids dissociation by the intermediary of the water formed from the ammonium phosphate. This is still only a hypothesis, but I wanted to let you know these results.

Mr. M. DETUNCQ (Péchiney-St.Gobain, France) : How do you control the level of ammoniation - continuously or discontinuously? How do you limit your temperature to 100°C ?

Mr. BERQUIN : We have tried to continue the directions in which we have been working since the start of our research on complex fertilisers. Since this time, we have always tried to have absolutely continuous processes. The present case is no exception: we pre-ammoniate continuously in the tanks comprising the first stage of the operation. Ammonia, acid and if necessary phosphate, in the case of reaction, are fed continuously into these tanks. Thus we have continuous flow of slurry available for feeding into the dry apparatus. In a number of trials we have split the length of the apparatus into several sections, each provided with an independent ammonia feed controlled by its own valve and rotameter, in order to have a fairly gentle final ammoniation to limit possible losses.

With regard to control of temperature at 100°C, there are several answers to this, varying according to the processes used. In many cases an autoregulation is involved, for if the temperature becomes too high ammonia fixation is no longer achieved. Consequently, the temperature is stabilised, but important ammonia losses can be observed in ammoniation. Another method used involves the control of the phosphoric acid concentration. Thus you will see from the

paper that for phosphoric acid alone, we have used a 42% acid. Our first trials did, in fact, take place with more concentrated acids, and we observed that the rise in temperature due to the high concentration of these acids prevented a good fixation of the ammonia. We therefore explored the zone of possible interesting concentrations and decreased the concentration used in practice to 42%, for at that level there was a good concordance between ammonia fixation on the one hand and moisture content on the other, leaving a minimum of moisture in the product emerging from the unit.

Finally, in processes which do not contribute much heat, although the amount of water present may be small, it is necessary to use additional heat. Most usually, we have done this by passing hot air directly over the bed - for in this way the amount of air needed is limited and subsequent scrubbing of the gases is rapid. In this case, it is very easy to regulate the temperature of the hot gases passing over the bed as a function of the results obtained. If necessary, one can even cool the material by this method.

Mr. V. SQUATRITI (Stà. Edison, Italy) : To what extent can the process you describe be considered as a modification of the process incorporating a spherodizer? I can see that you probably achieve a saving in the group of tanks, where it is no longer necessary to complete ammoniation to obtain the complete slurry. On the other hand, in the spherodizer itself the internal apparatus is simplified by the elimination of the vanes which were one of the principal features; but they are replaced by ammonia injectors. I should therefore like to know to what extent all this represents a benefit from the point of view of production costs.

Mr. BERQUIN : Our plant is not a spherodizer. A spherodizer is not used for chemical reactions: it is purely a drying unit. From the technical standpoint, the spherodizer is designed to create a curtain of granules falling within a current of hot air. Our unit is much more like a drum granulator in which there is a rolling bed and not a cascade of granules. Moreover, our unit is used for chemical reactions, since ammonia and, possibly, additional acid are fed into it. Consequently, it is an apparatus which resembles a spherodizer, but all our units resemble each other more or less: they have common parts. Also, we employ sprinkling in order to obtain thin layers, but the drying is not a true drying - it is a dehydration, a fixation of ammonia and a physical change resulting from the reactions occurring at this stage. I think therefore that it would be somewhat exaggerated to say that this is a spherodizer, even a transformed spherodizer.

As far as the advantages are concerned, there is on the one hand a saving in the wet process part by reducing the apparatus, and on the other hand, from the cost point of view, one should consider the saving in fuel and, in a general way, in the drying of the finished product. This was the object we sought to attain.

Mr. P. MORAILLON (Péchiney St.Gobain, France) : Do you prefer the ammonia injected into the ammoniating drum to be liquid or gaseous?

Mr. BERQUIN : So far we have used only gaseous ammonia, for it is obviously much easier to regulate than liquid ammonia. The rate of absorption is generally good. We are still in the preliminary stage, and our trials have taken very different directions. Consequently, we cannot talk of absolute values, but we generally succeed in maintaining about 90% absorption; i.e. 10% of the ammonia escapes in the gases emerging from the drum. Naturally, these gases are then scrubbed. Whenever possible, we prefer to use phosphoric acid for this scrubbing, or sulphuric acid if available.

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