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# THE INTERNATIONAL SUPERPHOSPHATE MANUFACTURERS' ASSOCIATION

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### NOTES ON THE MANUFACTURE OF FERTILISERS BY NITRIC

#### SOLUBILISATION OF PHOSPHATES,

by Y. Martin. (Cie. de Saint-Gobain).

The principle of solubilisation of phosphate by nitric acid, alone or in conjunction with other acids, is well known and has already received industrial application for a considerable time, especially in France.

However, only with the second world war and the resulting shortage of sulphur has the application of this principle become a necessity for us and has led to studies and practical application in the case of the majority of the important French manufacturers, as shown by the appearance on the market of increasing tonnages of compound fertilisers, where the phosphate, either in its entirety or in part, has been solubilised by nitric acid.

It must, however, not be assumed that this practical application has been arrived at in a simple manner. Those who have witnessed the years of study and toil know full well the difficulties encountered and the danger for a neophyte in under-estimating them. They know equally well, by the simple process of examining the products on the market, that not all manufacturers have arrived at the same level of improvement in their process either because they did not follow the same road and, by going a different way, they have arrived at a different result, or because, although going the same way, they were not able to go as far as other scientists proceeding in the same direction.

The difficulties to overcome are encountered from one end of the manufacturing cycle to the other: loss in nitrogen, frothing, corrosion, setting, balance of moisture, reversion, granulation, storage, etc.; these are only technical difficulties. In addition, the necessity of satisfying the multiple requirements of crops has stressed more particularly some of these difficulties and at the time it would be impossible to state that all manufacturers have been able to free themselves from technical limitations in order readily to satisfy agricultural needs.

On the contrary, by examining certain formulas it can be seen that they were conceived by concentrating to a greater extent on avoiding certain technical limitations, as yet imperfectly mastered, than on satisfying the actual needs of customers. Everybody is fully aware of the extent of capital

outlay necessitated by the construction of works for compound fertilisers; in addition, it is important to limit one's choice in the knowledge of the technical possibilities and the requirements of the customers. Nitric solubilisation is not, in fact, a universal panacea; if it results in a certain saving in sulphuric acid, it does not always lead to the most concentrated fertilisers, to satisfactory equilibria or to the lowest manufacturing costs.

We propose to review the various technical processes available and to define them as simply as possible from the chemical point of view, giving a rapid survey of the apparatus required. We intend stressing, in each case, both the composition and the grade of phosphates they produce. Equally, we propose to show for each formula and technical process the rate of utilisation of nitric acid, i.e., the percentage of the nitric acid actually used for the breaking down of the phosphate. It can, as a matter of fact, be stated that the interest of a process from the point of view of saving sulphuric acid is all the greater, the higher the rate of utilisation of nitric acid for breaking down the phosphate, and one can ask oneself whether, in those cases where the rate of utilisation of nitric acid is low, the process is worth while, and whether the simple manufacture, such as that of superphosphate, ammonium nitrate and compound fertilisers, which results in low manufacturing costs, does not retain a certain interest, at least from the important angle of cost price.

It goes without saying that our paper will only deal with the processes which have been proved by several years of industrial application.

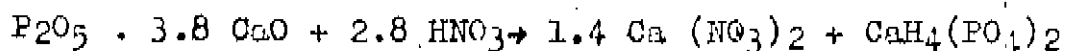
In order to simplify our paper, we propose to divide the different processes into two comprehensive categories: solid phase and liquid phase processes. The first results in products where the phosphoric acid is essentially water-soluble, the second leading very often to products where the phosphoric acid is in a citrate-soluble form.

A. Solid phase manufacturing process, resulting in fertilisers where the P<sub>2</sub>O<sub>5</sub> is in a water-soluble form.

(1) Purely nitric solubilisation.

In this field, pride of place must without doubt be given to the Lanza process which, to our knowledge, is the only process in the world where a purely nitric attack results directly, without concentration or drying, in a granulated compound of impeccable quality.

The chemistry of the process is very simple and can be summed up in the reaction:



The concentration of nitric acid is calculated in such a manner that the nitrate of lime formed crystallises with less than three molecules of water.

The basic fertiliser obtained is a granulated binary, containing 7.5 nitric nitrogen and 14 of P<sub>2</sub>O<sub>5</sub> soluble in water (15 soluble in citrate). It goes without saying that the same installations allow of producing a granulated ternary, the most current formula being 6 - 12 - 8.

In this process the saving in H<sub>2</sub>SO<sub>4</sub>, as compared with the manufacture of superphosphate, is obviously 100%, seeing that nitric acid is purely and simply replacing sulphuric acid. In the same way, the rate of utilisation of nitric acid for the breaking down of the phosphate, as defined above, is 100%.

The Lonza process has been working on an industrial scale for more than 20 years; it has been improved all the time. In its present form, the production of a typical unit attains 100 tons per day; an important development of this process appears to be certain in those countries where the shortage of sulphuric acid prevails and where the criterion of assimilability is water solubility.

(2) Mixed sulphuric-nitric solubilisation.

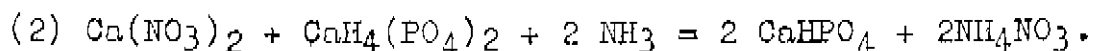
Seeing that the processes in this field form the subject of a paper by Mr. A. Constant of the Sté. des Usines Dior, we do not propose to expatiate on the corresponding technical aspects, but would confine ourselves to recalling that

- (a) these processes and the corresponding products derive a benefit from a far-reaching industrial and commercial application;
- (b) the processes have the advantage of being applied in simple installations of the type of certain superphosphate works;
- (c) the rate of utilisation of the nitric acid employed represents a 100% saving of sulphuric acid and about 65% as compared with the manufacture of superphosphate.

B. Liquid phase manufacturing process resulting in fertilisers where the P<sub>2</sub>O<sub>5</sub> is mainly in the form soluble in citrate of ammonia.

All the processes belonging to the second category endeavour to obtain in some way or other, after the attack by the acid, an acid slurry where the ratio  $\frac{\text{soluble CaO}}{\text{soluble P}_2\text{O}_5}$  is, at the most, equal to 2, or a slurry containing at the most as many nitrate of lime molecules as mono-calcium phosphate molecules.

This slurry is then treated with ammonia in such a manner as to obtain the following reaction:



As in the foregoing process, the chemistry of the above processes implies a very definite ratio of the grades of nitrogen and P<sub>2</sub>O<sub>5</sub> of the corresponding basic fertilisers.

- 1 of nitric nitrogen - 2 of P<sub>2</sub>O<sub>5</sub> in the Lonza process
- 1 of nitric nitrogen - 4 of P<sub>2</sub>O<sub>5</sub> in the Constant process

and, in this instance, according to reaction (2), 14 of nitric nitrogen and 14 of ammoniacal nitrogen to 142 of P<sub>2</sub>O<sub>5</sub> would equal approximately

and  $\left. \begin{array}{l} 1 \text{ nitric nitrogen} \\ 1 \text{ ammoniacal nitrogen} \end{array} \right\} \text{to } 10 \text{ of P}_2\text{O}_5$

This statement is important: As we have already mentioned at the beginning of this paper, the commercial and technical necessities lead to a deviation from the equilibrium, corresponding to reaction (2) and, consequently, to a considerable reduction in the rate of utilisation of nitric acid.

The ratio  $\frac{\text{soluble CaO}}{\text{soluble P}_2\text{O}_5} = 2$  is obtained by

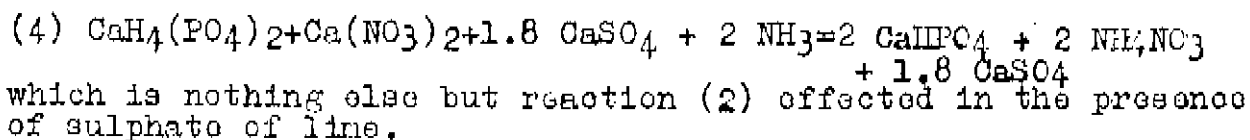
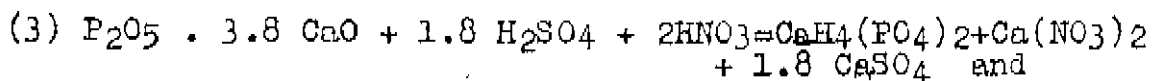
- solubilisation of a portion of the phosphate of lime in the form of sulphate of lime by adding sulphuric acid to nitric acid,
- by enriching the slurry in P<sub>2</sub>O<sub>5</sub> through the addition of phosphoric acid to nitric acid,

- by impoverishing the slurry by separating a considerable portion of the nitrate of lime formed during the attack of the phosphate with nitric acid.

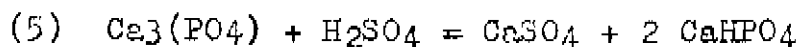
Hence we distinguish the following processes:

(a) Sulphuric-nitric solubilisation processes.

Generally speaking, the following reactions take place in these processes:



All the nitric acid used is finally found in the form of ammonium nitrate, and it is possible to say that these processes allow, in the main, of the indirect production of di-calcium phosphate by the action on the phosphate of half the quantity of acid of that used for the manufacture of superphosphate. Indirectly the following reaction is obtained:



and it is known that by direct action of sulphuric acid in smaller quantities one does not obtain di-calcium phosphate, but a mixture of mono-calcium and tri-calcium phosphate.

The interest in the processes of sulphuric-nitric solubilisation lies in the main in the saving of sulphuric acid, when solubilising phosphate, amounting to about 50%, as compared with the manufacture of superphosphate. This figure has been confirmed by an industrial application of several years' duration, during which the consumption of sulphuric acid per 100 kgs of solubilised  $\text{P}_2\text{O}_5$  has attained 105 kgs as against 210 in the manufacture of fertilisers with the same N and  $\text{P}_2\text{O}_5$  content, based on superphosphate.

This economy explains the development of this process both in France and in Germany.

It is, however, advisable not to lose sight of the fact that a saving of  $\text{H}_2\text{SO}_4$  is one thing and that the production of a fertiliser at a low production cost is another.

In the compounds, regularly placed on the market, the economy in  $\text{H}_2\text{SO}_4$  only represents in fact about 4% of the selling price.

It will be realised that, if the difficulties of this technical process were not all solved by the constant endeavour to lower production costs, the benefit to be derived from such a process would be purely nominal.

This would be the case with an installation involving a considerable capital expenditure or a heavy maintenance cost, even if it were simplified by installing standardised apparatus. This would also be the case with installations where, given the difficulties of realising reaction (2) (difficulties of introducing ammonia into the slurries, which thickens to a considerable extent as and when the precipitation of di-calcium phosphate occurs) a portion of  $\text{P}_2\text{O}_5$  would revert, whilst another would not be transformed and would remain in the form of mono-calcium phosphate.

This would finally be the case with installations where the saving in sulphuric acid would be offset by expenses in connection with power (energy for agitation in particular) or with fuel in the case where the heat, liberated by the reactions, would be inefficiently utilised. This latter point is of particular importance. The processes in question lead, in fact to a simultaneous production of di-calcium phosphate and ammonium nitrate, whereby the entire nitric acid used is transformed into nitrate. In order to attain the advantages of manufacturing di-calcium phosphate, it is not a question of concentrating on the manufacture of ammonium nitrate under conditions inferior to those in installations now regarded as typical models and working smoothly. These real difficulties have opened up a way for a technique, brought about by experience, and working to the satisfaction of the customers, where the benefit of the sulphuric nitric solubilisation is not purely nominal. We propose to give a fairly exact idea of the important reduction in capital outlay, plant and production cost of our process by indicating that we were able to apply it to works for the granulation of compound fertilisers on the basis of superphosphate of the standard type, without any alteration of buildings, without reduction in production capacity and with a higher content in nitrogen and P<sub>2</sub>O<sub>5</sub>.

The compositions of fertilisers, regularly manufactured by sulphuric and nitric solubilisation, ranged from 12 - 8 - 20 to 10 - 10 - 17, this latter formula corresponding to 11.5 - 11.5 - 11.5 in balanced fertilisers. We manufacture regularly a 10 - 10 - 15 fertiliser. In this fertiliser, the ratio  $\frac{N}{P_{2}O_{5}}$  is definitely higher than that which corresponds to reaction (2). Taking into account the sulphuric acid used, which must be regarded as taking a most active part in the breaking down of the phosphate, it is possible to say that in this fertiliser only 36% of the nitric acid used contributed to the breaking down of the phosphate.

A higher rate of use would imply a nitrogen content lower than that of P<sub>2</sub>O<sub>5</sub> and difficulties occurring during manufacture. It goes without saying that the P<sub>2</sub>O<sub>5</sub> content can be adjusted by the addition of phosphatic fertilisers, such as ammonium phosphate and di-calcium phosphate for example.

On the other hand, the compounds of the type 12 - 8 - 20, where the proportion  $\frac{N}{P_{2}O_{5}} = 1.5$  instead of 1, can be more readily produced, but correspond to a rate of utilisation of nitric acid still less than 24%.

As to the concentration of the fertilisers obtained, the balanced formula 11.5 - 11.5 - 11.5 leads to a gain of 4.5 fertiliser units as compared with the formula 10 - 10 - 10, obtained on the base of superphosphate.

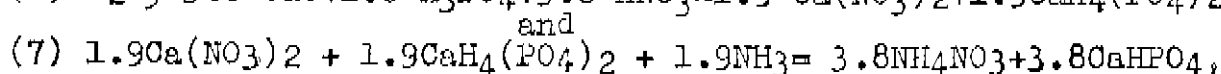
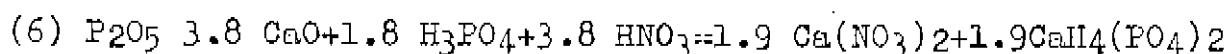
Summarising, it may be said that sulphuric-nitric solubilisation which we have applied in our installations permits the manufacture in one single works of: phosphate - HNO<sub>3</sub> 36 AB - H<sub>2</sub>SO<sub>4</sub> 60 AB - KCl, a fertiliser of the granulated type 10 - 10 - 15 with lower manufacturing costs and better production than in works specialising in ammonium nitrate and in superphosphate, and with a saving in sulphuric acid of 50%.

On the other hand, one cannot expect from sulphuric nitric solubilisation that which it cannot offer, particularly either a high rate of utilisation of nitric acid, or very concentrated fertilisers, or a varied scale of equilibria of fertiliser elements.

This induced us to study and to apply

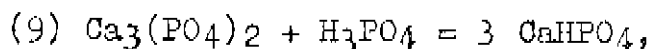
(b) Phosphoric-nitric solubilisation processes

Generally speaking, the following reactions are obtained in these processes:

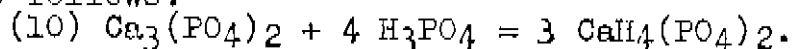


which is nothing else but reaction (2).

All the nitric acid used is obtained in the end in the form of ammonium nitrate, and it can be said that all these processes, generally speaking, permit the indirect production of di-calcium phosphate by the action on the phosphate of a quantity of acid, one quarter of that used in the manufacture of triple superphosphate and, indirectly, the following reaction is obtained:



whilst the typical reaction in the manufacture of triple super is as follows:



On the occasion of the preceding Congress, we had shown the progress made in the manufacture of phosphoric acid and hope to have contributed to the elimination of some of the unfavourable prejudices in regard to this manufacture.

At the same time Mr. Nordengren has shown, and quite rightly so, that the manufacture of triple super, in taking into account the saving made by the production of concentrated fertilisers, permits the delivery of a lower priced  $\text{P}_2\text{O}_5$  unit than that in ordinary super.

On taking into account that with the same quantity of phosphoric acid it is possible to treat four times as much phosphate by transforming it into dicalcium phosphate, the importance of the processes for breaking down with phosphoric and nitric acids is obvious.

From the point of view of economising sulphuric acid, the processes are exactly in the same category as the processes for the breaking down with sulphuric and nitric acids. As a matter of fact, even if the production of phosphoric acid is taken into account, the consumption of  $\text{H}_2\text{SO}_4$  per 100 kgs of solubilised  $\text{P}_2\text{O}_5$  is not greater, owing to the fact that certain impurities of the phosphate in the presence of phosphoric acid are not attacked. It goes without saying that, in the case where phosphoric acid is obtained by thermic treatment, the saving in sulphuric acid would amount to 100%.

From the point of view of utilising nitric acid, the processes of phosphoric-nitric attack make it possible to obtain equilibria N -  $\text{P}_2\text{O}_5$ , far richer in  $\text{P}_2\text{O}_5$ , which results in a better use of nitric acid - for example twice as high in the compound 10 - 15 - 20 than in the compound 11 - 9 - 20 - obtained by sulphuric-nitric solubilisation.

As to the type of fertiliser which can be obtained, the phosphoric-nitric solubilisation has the advantage of a greater elasticity than the sulphuric-nitric solubilisation, as it widens the range of the latter in an advantageous manner. By way of example, starting with the equilibrium N/ $\text{P}_2\text{O}_5$  = 1 corresponding to 10 - 10 - 17 sulphuric-nitric solubilisation, one passes to 12 - 12 - 20 (the former German Nitrophoska) phosphoric-nitric solubilisation, and it is possible with our technique to increase the  $\text{P}_2\text{O}_5$  content without difficulty to

10 - 15 - 20 via 12 - 15 - 18 for example, not to speak of the compounds which we have retained.

All these compounds contain about 45 fertiliser units per 100 kgs of fertiliser, as against 30 for compounds, based on superphosphate and 35 for those, obtained with sulphuric-nitric solubilisation. As with the 45% super, it can be seen what economies can be effected from the point of view of storage area, manipulation cost, transport and bagging. In addition, it has to be noted that all the compounds indicated can be increased, as far as ammonium phosphate content is concerned, by increasing the quantity of phosphoric acid used, which has the advantage, not only of obtaining more concentrated fertilisers, but, above all, of obtaining a higher content in ammoniacal N than in nitric nitrogen, which is not without interest as far as autumn is concerned.

For the breaking down of phosphate and its treatment with ammonia we have been able to construct an apparatus which permits both the sulphuric-nitric and phosphoric-nitric solubilisation or the mixed sulphuric-phosphoric solubilisation. The corresponding elasticity of the manufacturing unit allows of satisfying, so to speak, on demand, all the requirements of the customers.

According to the terms of this paper it remains for us to say a few words about the process of nitric attack followed by a separation of one portion of the nitrate of lime and of the treatment of the mother liquor with ammonia.

The processes have already been applied regularly in France prior to the war and have since developed in Belgium and Holland. They lead practically to the same compounds as the phosphoric-nitric solubilisation. The formula 20 - 20 regularly produced results, as a matter of fact, after the addition of potash in the 12 - 12 - 20 fertiliser, of which we spoke previously.

In the same way one obtains about 2/3 of "fatal" nitrate of lime with 13 ~~g~~ of nitrogen, containing 3/4 to 4 ~~g~~ of P<sub>2</sub>O<sub>5</sub>, which is perhaps somewhat difficult to assess commercially. On the whole, the average concentration of fertilisers obtained does not exceed 30 to 33 fertiliser units. This is not at all surprising; pure nitric solubilisation cannot result in concentrated fertilisers, seeing that it produces, of necessity, fertilisers which are richer in nitric nitrogen than in ammoniacal nitrogen, and that the nitric acid contains only 22% of nitrogen, whilst ammonia contains 82% of nitrogen.

Although these processes use only nitric acid, only one portion of the latter helps to break down the phosphate, the other being responsible for the formation of ammonium nitrate in the compound fertiliser obtained. It follows, therefore, that the rate of utilisation of the nitric acid, as defined by us, is of the order of 60%.

To conclude let us review on broad lines our survey:

- Two processes incorporating the purely nitric attack, one with separation of nitrate of lime and resulting in P<sub>2</sub>O<sub>5</sub> being in the form of di-calcium phosphate, the other without separation of nitrate of lime, resulting in water-soluble P<sub>2</sub>O<sub>5</sub>.
- Processes of mixed solubilisation, sulphuric-nitric or phosphoric-nitric; the sulphuric-nitric solubilisation should, in our opinion, only be considered as the first stage, the advantages of phosphoric-nitric solubilisation being much greater.

He who says "Phosphoric-nitric acid" says phosphoric acid. The manufacture of phosphoric acid is after all only the ultimate stage of the sulphuric acid - phosphate reaction. We trust that our paper has not greatly exceeded the range of questions which interest the manufacturers of superphosphate.