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NOTES ON THE PRODUCTION OF SUPERPHOSPHATE, NITRATES OR PHOSPHO-NITRATES AND THEIR DERIVATIVES

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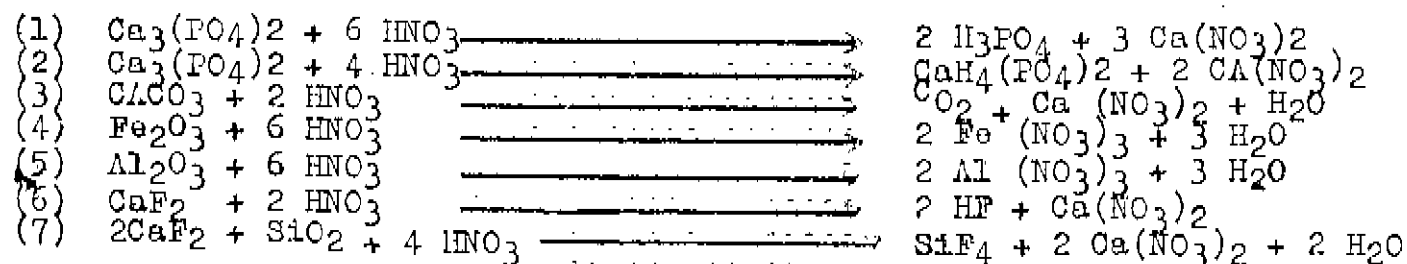
I. FOREWORD. The world shortage of sulphur sets the superphosphate manufacturers a difficult problem both in regard to the quantity to be produced and the cost price. The solution which consists of substituting nitric acid either partially or completely for sulphuric acid when attacking phosphates is interesting from both these points of view seeing that the nitrogen introduced is obtained in the form of nitrate of lime. It is more economical to produce this nitrate on the basis of phosphate than on that of carbonate of lime.

The aim of the present exposé is to indicate the conditions for the transformation of tri-calcium phosphate into mono-calcium phosphate according to the processes worked out by Société Anonyme des Usines Dior to form nitrated superphosphates called "nitro-phosphates" or "phospho-nitrites".

II. SOME CONSIDERATIONS GOVERNING MANUFACTURE.

We do not propose to recapitulate the well known reactions of sulphuric acid and phosphate.

The principal reactions possible between phosphate rock and nitric acid are as follows:-



The two last named only occur at a high temperature and not at 35 or 40° centigrade.

In the case of solubilisation by a mixture of sulphuric and nitric acids or by nitric acid alone, precaution must be taken that this limit of temperature is not exceeded because the only material suitable for this kind of manufacture, namely stainless steel with 18% Cr, 8% Ni and 2% Mo is very rapidly corroded by fluorine compounds. This limitation of temperature, in addition, results in a considerable saving of acid.

Another reason for keeping within this limit lies in the consideration of vapour pressures of the acids used which often contain large proportions of N_2O_4 . Experience has shown that during manufacture losses of nitrogen are maintained at less than 1% if the reaction temperature is less than or equal to 35° centigrade, 40° being a tolerable maximum in certain circumstances.

The first condition to observe is the following:

THE REACTION TEMPERATURE MUST BE LIMITED TO 35/40° CENTIGRADE AS LONG AS NITRIC ACID REMAINS FREE.

In ordinary superphosphate the salts formed - mono-calcium phosphate and sulphate of lime - are not hygroscopic. Knowing the loss of moisture during manufacture it is easy to determine the minimum concentration of sulphuric acid to be used.

It is not the same with phospho-nitrates, the nitrate of lime which can crystallise with four different hydration values 0 - 2 - 3 - 4. The range of hygroscopicity of the tetra-hydrate varies from 56 - 36 according to temperature, a figure which is too low for a satisfactory appearance. As the moisture can be readily regulated, seeing that the loss is almost nil during manufacture, it is easy to determine for each type of phosphate rock the degree of hydration desired and to find out the behaviour of the product.

For Morocco phosphate containing 33% P_2O_5 , for example, when disregarding the nitrates of iron and aluminium and taking into account the normal hydration of mono-calcium phosphate, the following results are found for the hydration of nitrate of lime according to the concentration of the nitric acid used:

Concentration of acid	Number of molecules of $Ca(NO_3)_2$ formed for 1 of $CaH_4(PO_4)_2$	Hydration of $Ca(NO_3)_2$
70%	3.25.	tri-hydrate
80%	-	0.15 mol. anhyd. 3.15 Di-hydrate
90%	-	1.95 mol. anhyd. 1.3. di-hydrate

Hence the second condition, borne out by experience for temperate climates:

THE CONCENTRATION OF THE ACIDS USED MUST BE SUCH THAT THE HYDRATION OF THE NITRATE OF LIME FORMS EITHER LESS THAN OR, AT MOST, EQUALS 2 MOLECULES OF WATER.

In the case of an attack by sulphuric and nitric acids the concentration of the two acids depend on each other; with concentrated sulphuric acid, for example, the concentration of nitric acid may diminish to 50 or 60%. With nitric acid alone, the concentration is calculated as a function of the above condition.

For a phosphate rich in iron and alumina oxides, the degree of hydration of the corresponding nitrates has also to be calculated.

The reserve of sligaty thus allowed abviate all the difficulties in connection with bagging, transport and spreading.

Storage in sheds does not present any difficulty, if, as mentioned below, some of the heat due to the reactions and, above all, to crystallisation does only escape until after storage.

III. PROCESS OF MANUFACTURING PHOSPHO-NITRATES

As we have seen, the composition of the phosphate governs the concentration of the acid or acids used. There is, therefore, no difficulty if a sufficiently concentrated acid is at one's disposal.

It is not the same with regard to the maintenance of the reaction temperature at 35° centigrade because the volume of liberated heat is considerable.

With superphosphate, the same method could be applied in all climates, but for phospho-nitrates it is advisable to provide for different means of cooling according to the surrounding temperature in the manufacturing plant.

With a surrounding temperature of - 30° centigrade the means would be small or nil; they would be very considerable with those of + 20 or + 30.

As will be seen further below, the process requires the installation of special means of cooling for only part of the heat evolved by the actual reactions or crystallisations resulting therefrom; it varies practically from 50 to 10% according to the manner of solubilisation used in temperate climates.

The remainder of the heat produced is lost by radiation.

This process applies to all methods of solubilisation: with nitric acid alone or with sulphuric and nitric acids acting either together or separately.

The whole of the reactions can be divided into three successive phases:

(a) In the first, all the acid is introduced and about 2/3 of the phosphate in such a manner as to obtain reactions (1) - (3) - (4) - (5). The operation is carried out in a trough with cooled walls whose capacity, for the same tonnage to be produced would vary, according to the climate. The liquid slurry resulting from previous reactions between the same constituents revolve in this trough; the phosphate and the acid or acids are introduced continuously at certain selected points, a corresponding quantity being withdrawn continuously through an outlet which is as far as possible from the points where the raw materials enter. Agitators prevent the slurry from frothing due to the liberation of CO₂.

(b) The product leaving the outlet is mainly composed of free phosphoric acid, non-hydrated nitrate of lime, sulphate of ammonia - if sulphuric acid is employed - and of the gangue of phosphate which readily remains in suspension. To this is added, in a second trough, the remainder of the phosphate and the whole undergoes a brief mixing with a continuous motion towards the outlet where the material is in an almost solidified state.

(c) In order to break up the mass leaving the second trough, the natural tendency of phospho-nitrate to granulate is utilised in a trough of considerable length, equipped with paddles, producing an energetic mixing and a slight movement towards the outlet. Crystallisation is accelerated by adding a previously finished cold product which has been reduced to the fineness required.

The granules formed are then passed over two superimposed vibrating screens. The oversize granules are re-crushed and re-cycled with the fines in the granulator. The medium-sized granules

constituting the marketable material are sent to the store. They harden very rapidly. The three apparatus are arranged one above the other so that the flow from one to another is effected by gravity. From the entry to the outlet of the apparatus the duration of the flow is about one hour.

With this method, only the trough of the first phase has to be cooled up to the outlet where the acid or acids of the attack are neutralised. The engendered heat is completely or partially counteracted by the heating of the raw materials introduced and for the remainder, by the circulation of water or the sprinkling of water round the walls. It is also possible to cool the acid. As indicated above, the required amount of cooling can be readily calculated in each case. In hot weather it is advisable also to cool the finished product before re-cycling it in the circuit.

As purely nitric solubilisation forms the subject of another paper, we propose to speak especially of the mutual action of nitric and sulphuric acids which is interesting because of the products obtained and because it requires less concentrated nitric acid when 78% or stronger sulphuric acid is used.

Two cases present themselves:

- (1) the two acids are mixed before use -
The reactions are extremely marked and precautions have to be taken to avoid the generation of nitrous vapours owing to the rise in temperature. So long as the sulphuric acid remains free, it decomposes the nitrate of lime, giving rise to regenerated nitric acid and sulphate of lime. But the latter does not adhere to the phosphate grains as in the case of the manufacture of superphosphate and this enables the reaction to carry on actively until the attack is completed.
- (2) The two acids react separately -

If the manufacturer has at his disposal the two acids separately an existing superphosphate unit, it is of particular interest to treat the phosphate in two phases instead of attacking it with a mixture of sulphuric and nitric acids.

First, the sulphuric acid acts upon a portion or the entire phosphate and the intermediary product thus obtained is then treated with nitric acid. This product may also be ordinary superphosphate coming from storage; In that case the apparatus described above suffice. The superphosphate and one portion of the phosphate are introduced into the first trough the other operations following the same conditions as in purely nitric solubilisation.

The P_2O_5 of the mono-calcium phosphate is transformed into free phosphoric acid and enters again in its original state into the succeeding operations. This reaction evolves very little heat.

The apparatus must be completed by a continuous mixer and a cooling tube if the attack by sulphuric acid is carried out in the plant. When treating the greater portion of the phosphate, the reaction is less pronounced, especially if the acid is cooled. Fluorine compounds are not liberated, hence the considerable saving in sulphur.

IV. APPARATUS. The apparatus is common to all types of attacks described above.

The trough for the first phase as well as the agitators are in stainless steel 18% Cr, 8% Ni and 2% Mo. It takes the usual form of two rectangles bracketed together along one of the long sides with a communication at each of their ends. A double jacket is used for cooling.

The second phase takes place in a trough of the same metal of a semi-cylindrical shape along the axis of which is fitted an agitator with paddles which produce a radial and axial movement so that the products circulate upwards and downwards. This trough is not cooled.

The third phase takes place in a third trough of ordinary sheet steel of the mixer type with two parallel shafts with paddles producing a radial and axial motion, as in the case of the trough described above. An energetic mixing is necessary in order thoroughly to mix the upstream end where the recycled finished product is added to the product leaving the second trough.

The three troughs are arranged one above the other so that from the inlet to the outlet the materials circulate by gravity. The remainder of the apparatus, distribution screening and manipulation are similar to those installed in all fertiliser works.

V. PRODUCTS OBTAINED

With the methods indicated it is possible to obtain quite a range of products.

The nitrogen and P_2O_5 content depend upon the content of the phosphate in the materials used for this reaction.

With a 33% Morocco phosphate and with a rate of attack of 90.95%, it is possible to obtain, by varying the proportions of sulphuric and nitric acids, quite a range of products where the ratio $\frac{P_2O_5}{N}$ varies practically from 2 to 4 viz:-

Nitric nitrogen	8%	water-soluble	P_2O_5	15.5%	citrate-soluble	0.5%	or
"	"	4%	"	15.5%	"	"	0.5%

By suppressing sulphuric acid, which can be effected in the manufacturing process mentioned in the first place, a 8 - 16 fertiliser is obtained. It should be noted that the production of the apparatus is twice as large as in the case of fertiliser 4 - 16 which is obtained by solubilisation with half the quantity as sulphuric acid the other as nitric acid, by separate action of the two acids.

The storage in sheds is very satisfactory and can be continued for a long time seeing that the presence of both sulphate of lime and nitrate of lime is very advantageous.

VI. COMPOUND FERTILISERS ON THE BASIS OF PHOSPHO-NITRATE.

(a) Binaries with nitrogen partly in a nitric and partly in an ammoniacal form are obtained by the addition of sulphate or phosphate of ammonia.

Nitrate of ammonia is not suitable because it forms, with the nitrate of lime, a double salt $1 NH_4NO_3 - 5 Ca(NO_3)_2 - 10 H_2O$ which is extremely hygroscopic.

(b) Ternaries.

Nitrate of lime does not mix well with chlorated compounds, but very well with phosphate, sulphate and nitrate of potash. The mixture $2NH_4NO_3 - 1 K_2SO_4$ undergoes a double decomposition to form $2 KNO_3 - 1 (NH_4)_2 SO_4$ which also gives good results.

Similarly, it is possible to use bi-sulphate of ammonia and potash which are more easily produced than the corresponding neutral chemicals by themselves.

Certain processes which do not fall within the framework of this study and which form the subject of another paper permit the economic production of ternaries very rich in fertiliser elements and where the P_2O_5 is almost entirely water-soluble.

In the production of all these compound fertilisers the apparatus described above are used. As in the case with phospho-nitrates, these fertilisers are obtained in granulated form without drying.

VII. APPLICATION TO CROPS

It appears to be well demonstrated that the nitrate of lime contained in the phospho-nitrates or their derivatives disappears less quickly from the soil than when spread by itself. This results in a certain saving of nitrogen and a better action on the plants and those effects are still more noticeable ^{with the} products of sulphuric-nitric solubilisation.

Applied in equal quantities, the compound fertilisers based on phospho-nitrates have an action superior to their homologues produced with ordinary superphosphate. The reason for this lies probably in the fact of the intimate association between the two or three salts: nitrate, phosphate and sulphate of lime.

The phospho-nitrates based on a nitric solubilisation alone are recommended as spring fertilisers. The others can be applied more or less on the same conditions as superphosphate.

VIII. CONCLUSIONS

- (a) It is possible to manufacture economically fertilisers on the basis of water-soluble phosphoric acid by substituting nitric acid for sulphuric acid either completely or partially and to counteract the lack of sulphur.
- (b) The products obtained by this substitution are very suitable for the manufacture of compound or complex fertilisers.
- (c) All these products give excellent results when applied to crops, probably owing to the presence of nitrate of lime the apparent solubility of which is diminished by the fact that it is coated or intimately mixed with the other constituents.
- (d) Because of the precautions mentioned above, the fertilisers reveal a better behaviour than the extent of their hygroscopicity in the laboratory would indicate and can be stored, distributed and spread without special precaution other than the use of bags which are water-proof.