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PROCESS FOR THE MANUFACTURE OF SUPERPHOSPHATE

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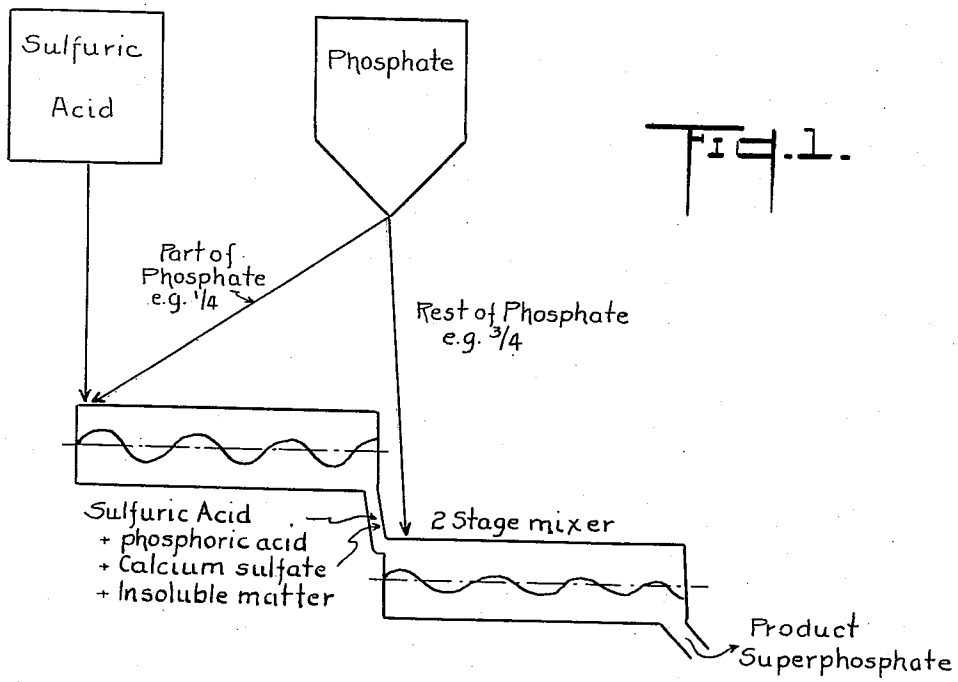


Fig. 1.

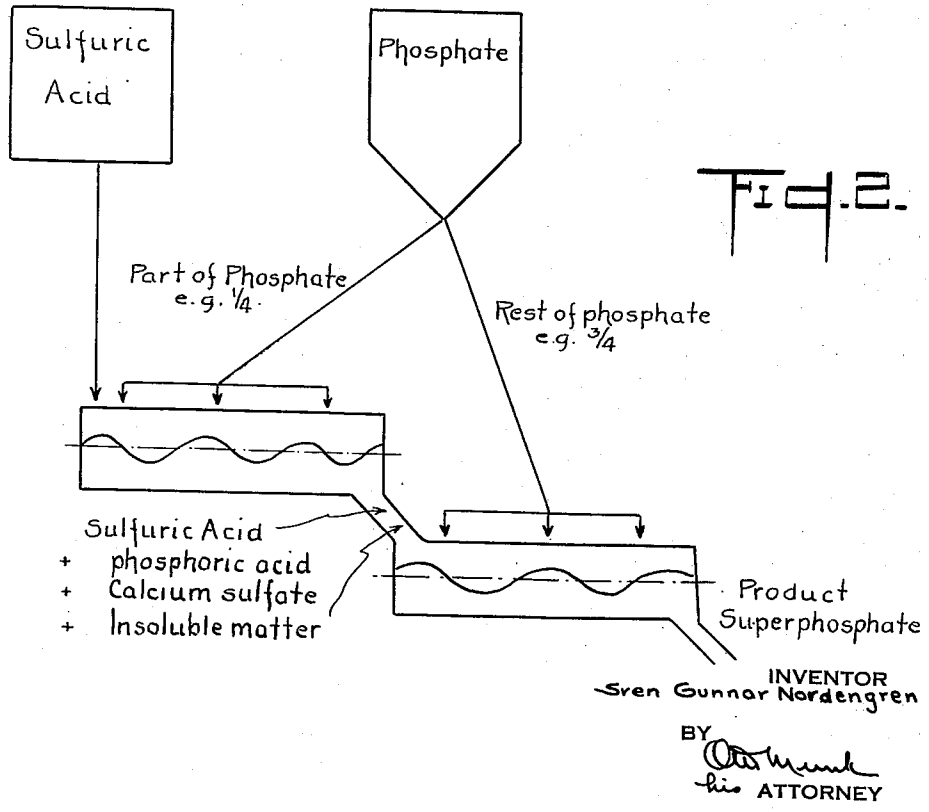


Fig. 2.

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PROCESS FOR THE MANUFACTURE OF SUPERPHOSPHATE

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7 Claims. (Cl. 71—40)

This invention relates to a process for the manufacture of phosphoric-acid-containing fertilizers from a phosphoric-acid-containing material and sulphuric acid with intermediate formation of phosphoric acid.

If in this sense a raw phosphate is decomposed with sulphuric acid in order to prepare a water-soluble superphosphate therefrom the transformation summarily proceeds between tricalcium phosphate and sulphuric acid according to the formula:

(1) $Ca_3(PO_4)_2+2H_2SO_4=2CaSO_4+CaH_4(PO_4)_2$

The tricalcium phosphate is converted by the sulphuric acid to monocalcium phosphate and calcium sulphate.

The above described transformation proceeds in two individual reactions, which are partially superimposed. In the first reaction the sulphuric acid acts upon a part of the tricalcium phosphate with formation of calcium sulphate and phosphoric acid:

(2) $2Ca_3(PO_4)_2+6H_2SO_4=6CaSO_4+4H_3PO_4$

The phosphoric acid so formed acts upon further quantities of tricalcium phosphate with formation of monocalcium phosphate:

(3) $Ca_3(PO_4)_2+4H_3PO_4=3CaH_4(PO_4)_2$

At the same time small quantities of dicalcium phosphate are formed. A small part of tricalcium phosphate remains undissolved and the corresponding quantity of phosphoric acid (from Equation 2) remains behind in the product in the form of free phosphoric acid. The sum of the two Equations 2 and 3, however, corresponds substantially to the course of the reaction taking place in the production of superphosphate (Equation 1).

In the production of double superphosphate the decomposition reaction is divided into two parts, phosphoric acid and calcium sulphate being first produced, the latter separated, and the resulting phosphoric acid employed for the decomposition of fresh quantities of raw phosphate.

The several steps of the present invention have been illustrated diagrammatically in the accompanying drawing, in which, Fig. 1 is a diagrammatic view of one mode of operation; and Fig. 2 is a diagrammatic view of another mode of operation.

According to the present invention the process is carried out in such a way, that the reaction in which phosphoric acid is formed, and the reaction which results in the formation of the phosphoric-acid-containing fertilizer, are carried out for one part of the initial phosphoric-acid-containing material separately in regard to time and space, without substantial quantities of the compounds formed by the reaction during the process of manufacture being separated. In the first stage of the process an excess of sulphuric acid is employed, and this excess is then directly converted into the end product in the second stage.

In the first stage, therefore, i. e., in the production of the phosphoric acid, the process is carried out with a deficiency of a phosphoric-acid-containing raw material, for example raw phosphate, i. e. with an excess of decomposition acid over the quantity necessary for the production of phosphoric acid, and in the second stage a correspondingly larger quantity of the raw material (phosphate) is introduced, for example into a mixing screw device.

Thus, for example, the operation may with advantage be carried into effect by introducing in the first stage only about 30% of the phosphate corresponding to the total amount of sulphuric acid, and making up this deficiency by introducing about 70% of the phosphate in the second stage, the process being, accordingly, only separated with regard to space and time with respect to a part of the total phosphate, thus in the aforementioned case with respect to 15+45=60% of the total quantity. The remaining 55% are then directly converted to the end product in the second stage in the manner hitherto usually adopted in the art.

This method of operating has proved to be particularly advantageous in cases, where it is desired to employ more concentrated sulphuric acid than hitherto, and accordingly a somewhat more viscous paste is obtained in the first stage. This method of operating further proves to be advantageous particularly in the case of phosphates which are relatively difficult to decompose.

With respect to the hitherto customary one-stage method of producing superphosphate the present process offers a great number of advantages. Thus in the first stage the decomposition is carried out rapidly and thoroughly, because it can take place in a liquid or relatively liquid medium. Moreover, in the first stage relatively coarse calcium sulphate crystals are also formed, which may then serve in the second stage as a basis or nucleus for the freshly formed crystals of calcium sulphate.

It has been further found, that the advantages of carrying out the decomposition in stages as

described above can be still further increased by carrying out in stages the reaction in which free phosphoric acid is first formed, or the reaction in which this phosphoric acid is converted by means of further raw material, for example raw phosphate, to the final product, or both reactions. Thus, for example, the operation may be carried into effect by adding the quantity of raw phosphate which is required for the first stage, in which free phosphoric acid is formed, to the decomposition acid in several individual portions, instead of adding the entire quantity at the start. A similar procedure may also be adopted in the second stage of the process, in which the mixture of phosphoric acid and the salt of the decomposition acid, for example calcium sulphate, obtained in the first stage, is allowed to react with fresh raw phosphate in order to obtain the final product.

If, for example, the production of superphosphate is regarded as described by formula in the initially mentioned formula, the following reaction will take place according to the described method of operation:

The quantity of 2 mols of tricalcium phosphate, necessary according to Equation 2, is not immediately mixed with the 6 mols of decomposition sulphuric acid, but in several successive portions. A similar procedure may be followed in the second stage, which proceeds in accordance with Equation 3, by introducing the quantity of tricalcium phosphate which is to react with the phosphoric acid formed in the first stage, viz: 1 mol. of $Ca_3(PO_4)_2$ per 4 mols of H_3PO_4, in successive individual portions, instead of in one portion at the start.

Such a method of operating is accompanied by various special advantages. The decomposition is above all improved thereby. The first portions of the phosphate in Equation 1 come into contact with a larger quantity of decomposition acid and the formation of crust, for example of calcium sulphate, on the phosphate grains is thus to a great extent avoided. Further, the subsequent portions of phosphate, for example in the production of superphosphate, contact with already formed calcium sulphate crystals, which serve as crystallization nuclei. A further advantage is a better elimination of acid gases, such as carbon dioxide and hydrofluoric acid compounds. In the second stage also, the first portions of phosphate contact with more acid (phosphoric acid) than when the entire quantity of phosphate is added, whereby the decomposition is likewise facilitated.

The effect of all these special advantages is, that at the end of the second stage a very satisfactorily decomposed and relatively dry product is obtained, since in the described method of operating the evaporation of water is also promoted. The physical form is also particularly good, i. e. the product is decidedly granular and particularly satisfactorily strewable and contains a larger quantity of utilizable phosphoric acid per unit weight and volume than the products formed by the ordinary processes of manufacture.

According to a particular embodiment of the invention the operation may also be carried out in such a way, that in the first stage the phosphoric-acid-containing raw material is brought into reaction substantially only with phosphoric acid, preferably by introducing the raw material into the upper part of the decomposition container and the sulphuric acid into the lower part.

If the phosphoric-acid-containing raw material, for example raw phosphate, in the first stage comes into reaction substantially only with the phosphoric acid, a soluble phosphate is intermediately formed, for example monocalcium phosphate, which can then in turn be subsequently converted by the decomposition acid, for example sulphuric acid, into phosphoric acid. By this method of operation the decomposing action and the quality of the end product can be still further enhanced.

The same principle in sense of counter-current can also be carried out, for example, by performing the first stage of the process in a mixing screw device, in the beginning part of which the phosphate is added, the sulphuric acid being added at a certain distance therefrom.

The above described method may be carried out in various types of apparatus. Thus, for example, it is possible to use an apparatus, which uses for the first stage several stirring containers, connected in series, and for the second stage a mixing screw device. In each of these containers a part of the phosphate necessary for the first stage is introduced. The second stage may be then either carried out as described above in a mixing screw device, into which the entire quantity of the phosphate may be introduced at once, or this quantity may also be introduced in portions at several spaced regions of the mixing screw device. The alternative procedure may, however, also be followed, which consists in carrying out the entire decomposition process, i. e. the first and second stages, in one or more mixing screw devices, connected in series, into which the phosphate is introduced in portions at different places. Such an apparatus is particularly easy to supervise and control and takes up only a small space.

As compared with the former methods for producing superphosphate this embodiment as well as the first described embodiment also offers the advantage of being capable of being operated continuously.

What I claim is:

1. A process of preparing superphosphate, which comprises mixing in a first step phosphate rock with sulphuric acid of relatively high concentration in great excess over that required for the decomposition of all the phosphate rock to phosphoric acid, and thereupon reacting in a second step the resulting unseparated mixture of phosphoric acid, sulphuric acid, calcium-sulphate, and undecomposed phosphate rock residue, with enough additional phosphate rock to form monocalcium-phosphate and calcium-sulphate in the ratio found in superphosphate.

2. A process according to claim 1, wherein the reaction of the first step is divided into several stages by introducing the corresponding quantities of the phosphate rock in portions and at different points into the reaction mixture.

3. A process according to claim 1, wherein the reaction of the second step is divided into several stages by introducing the phosphate rock in portions and at different points into the reaction mixture.

4. A process according to claim 1, wherein each of the two steps is divided into several stages by introducing the corresponding quantities of the phosphate rock in portions and at different points into the reaction mixtures.

5. A process as set forth in claim 1, in which the two steps are carried out continuously during the advancement of the reaction ingredients through at least one mixing device, the said phos-

phate rock being introduced into said device at two spaced regions thereof.

6. A process as set forth in claim 1, in which the two steps are carried out continuously during the advancement of the reaction ingredients through a plurality of successive mixing devices arranged in series, the said phosphate rock being introduced into said devices in separate portions.

7. A process as set forth in claim 1, in which the two steps are carried out continuously during the advancement of the reaction ingredients through a plurality of two or more successive screw mixers arranged in series, the said phosphate rock being introduced into said mixers in separate portions.

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