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PROCESS OF PREPARING A FERTILIZER

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The present invention relates to a process of preparing a highly valuable fertilizer from crude phosphate which, as is known, contains phosphoric acid in a non-assimilable form, i.e. in a form insoluble in citrate, and, moreover, contains more or less large quantities of calcium carbonate, calcium fluoride and silicic acid.

According to the present invention a mixture consisting of crude phosphate, ferrophosphorus and an alkali metal compound, preferably alkali carbonate is heated in an oxidizing atmosphere to a temperature of at least about 1100° C, suitably 1250° C–1350° C. In that case the quantities of ferrophosphorus and alkali metal compound to be applied, while assuming the known formation of tri-alkali-phosphate from the two constituents, must be proportioned in such a manner that the lime present in the crude phosphate and not bound as phosphate (inclusive of calcium fluoride) is transformed into tricalcium phosphate.

It is possible—but could not be ascertained by experiment—that first a reaction of the ferrophosphorus with the alkali metal compound occurs so as to obtain a phosphate-containing intermediate product, for instance in known manner an alkali phosphate which, on raising the temperature, acts upon the crude phosphate. The formation of an intermediate product consisting of tri-alkali-phosphate cannot forthwith be expected because the product consisting of ferrophosphorus and an alkali metal compound is present in an intimate mixture with an excess of crude phosphate.

The roasted material leaving the furnace consists of a product which is free from phosphide and contains phosphate and wherein all the phosphoric acid is present substantially completely in an assimilable form, i.e. in a form soluble in citrate.

The quantities of ferrophosphorus and alkali metal compound to be mixed with the crude phosphate in the starting mixture are preferably so high that—while assuming that the entire phosphorus contained in the ferrophosphorus is transformed into alkali phosphate—the lime present in the crude phosphate and not bound in the form of phosphate, calcium fluoride being included, if desired, may be transformed into tricalcium phosphate. It has been found that if there are used crude phosphates rich in silicic acid (containing more than 4 per cent. of SiO_2), such as for instance the Pebble phosphate containing 5–10 per cent. of SiO_2, it is sufficient for obtaining a perfect fertilizer to add the mixture of ferrophosphorus and alkali only in such a quantity that it amounts only to about 60–70 per cent of that quantity which is theoretically required for transforming the available lime into tricalcium phosphate, whereas in the case of crude phosphates poor in silicic acid (less than 4 per cent. of SiO_2) the theoretically expected mixture has to be added, in other words equal portions of crude phosphate poor in silicic acid in comparison with crude phosphate rich in silicic acid require a higher addition of a mixture of ferrophosphorus and alkali. According to another embodiment of the present invention this increased use of additional substances is avoided by adding to the crude phosphate poor in silicic acid such a quantity of silicic acid, if desired in the form of crude phosphates rich in silicic acid or in the form of ferrophosphorus containing silicon that the content of silicic acid in the starting mixture is between about 5 and 10 per cent. by weight.

The quantity of ferrophosphorus applied must, however, always be at least so large that the portion of phosphorus added, in the form of P_2O_5, is at least about 5 per cent. of the total quantity of the crude phosphate to be worked up. Smaller additional quantities of ferrophosphorus involve an incomplete elimination of the fluorine present in the crude phosphate.

In the process according to the present invention it has been found to be necessary to choose so large a portion of alkali metal compound, preferably applied in the form of alkali carbonate, in the material to be roasted, so that in the final product about 0.55 to 0.75 mol, preferably 0.60 to 0.70 mol of alkali oxide are present, calculated upon 1 mol of P_2O_5. It is necessary to observe also this additional range of the alkali to be applied so as to attain a complete elimination of the fluorine from the starting mixture. Furthermore, under these conditions of the process there results the surprising fact that in many cases (compare Examples 2, and 5 hereafter) a considerably smaller quantity of alkali (about 75 per cent) in the starting mixture suffices than would theoretically be necessary for transforming the phosphorus present in the ferrophosphorus into trialkali phosphate. This fact is based upon the observation that the alkali phosphate probably formed at the beginning of the reaction further reacts at once with the lime not bound to phosphoric acid with formation of tricalcium phosphate, whereby the alkali oxide which is set free may react with further quantities of ferrophosphorus.

Sometimes the content of silicic acid in the starting mixture, for instance due to the use of crude phosphate rich in silicic acid and ferrophosphorus rich in silicon may become so high that at the temperatures of the furnace undesired softening phenomenae of the starting mixture occur. In this case it is suitable according to the invention to add to the starting mixture lime or clay in such a quantity as has been proved to be practical by experience, preferably so large

an amount that a softening of the material to be roasted does not occur up to temperatures of about 1450°C.

There is no hindrance to partly substitute for the ferrophosphorus present in the starting mixture phosphoric acid, alkali-ortho-phosphate, alkali-meta-phosphate or alkali-pyro-phosphate or such salts containing phosphoric acid as are capable of binding the lime which is present in the crude phosphate, but not yet linked to phosphoric acid; such salts are for instance calcium monophosphate or calcium diphosphate.

According to a suitable method of carrying out the process of the invention an intimate mixture of finely ground crude phosphate on the one hand and ferrophosphorus and fine-grained sodium carbonate on the other hand, calculated according to the statements given above, is moistened with water to such an extent that the mass may be agglomerated so as to form small globular lumps of about the size of a pea. This reaction mixture is introduced into the upper, non-heated part of a slightly inclined revolving furnace and slowly conducted towards the fuel which enters from below and is suitably fed with such an excess of air that the escaping gases of combustion still contain about 1 to 2 per cent of oxygen. The temperature in the hottest part of the furnace is at least 1100° C, preferably 1250° C, and must not exceed 1350° C.

By the process of the present invention it is possible to produce from crude phosphate a matter useful as fertilizer simply in one single operation while simultaneously using ferro-phosphorus for which other possibilities of use exist only to a small extent.

The following examples illustrate the invention:

(1.) 2.46 kilos of ferrophosphorus containing 26.5 per cent of phosphorus are mixed with 4 kilos of sodium carbonate and soaked with water. After having added a mixture of 30 grams of finely ground Pebble crude phosphate (32.9 per cent of P_2O_5, 47.9 per cent of CaO, 7.3 per cent of SiO_2, 3.7 per cent of F) and 2 kilos of sodium carbonate the mass is vigorously kneaded. The content of water of the mass is to be so high that the kneaded mixture does not crumble. The mixture thus pre-treated is conducted to a granulation worm from which granulated bodies of a diameter of about 2 to 6 mm are obtained. Without having been previously dried the granulated bodies are then continuously introduced into the upper non-heated end of an inclined, revolving furnace and they gradually reach the hotter zones of the furnace. The revolving furnace is heated by means of fuel gases or burning oils which are blown in at its lower end with such an excess of air that the gas leaving the furnace still contains about 2 per cent of oxygen. The maximum temperature in the furnace amounts to 1250° C. When passing the furnace (50 to 60 minutes of sojourn) the granulated bodies maintain their form and do not tend to adhere at the walling of the furnace. The roasted product consists of

	Per cent
P_2O_5	33.85
CaO	41.20
Na_2O	9.65
Fe_2O_3	7.88
F	0.03
SiO_2	5.71

Residue: various metal oxides contained in the crude phosphate as impurities.

97.6 per cent of the phosphorus pentoxide present are soluble in citric acid, 96.9 per cent are soluble in citrate.

(2.) A mixture of 15 kilos of Pebble phosphate, 15 kilos of Morocco phosphate (34.5 per cent of P_2O_5, 49.6 per cent of CaO, 3.75 per cent of SiO_2 and 4.2 per cent of F), 6 kilos of sodium carbonate and 3.3 kilos of ferrophosphorus (containing 24 per cent of phosphorus and 1.45 per cent of silicon) is pre-treated and roasted as described in Example 1. The product leaving the furnace contains

	Per cent
P_2O_5	34.02
CaO	40.09
Na_2O	9.23
Fe_2O_3	8.67
F	0.05
SiO_2	5.43

Residue: various metal oxides contained in the crude phosphate as impurities.

97.7 per cent of the phosphorus pentoxide are soluble in citric acid, 95.4 per cent are soluble in citrate.

(3.) A mixture of 30 kilos of Morocco phosphate (34.5 per cent of P_2O_5, 49.6 per cent of CaO, 4.2 per cent of F, 3.75 per cent of SiO_2), 6 kilos of sodium carbonate and 5.1 kilos of ferrophosphorus (containing 25.6 per cent of phosphorus and 0.3 per cent of silicon) is treated as described in Example 1. The roasted product consists of

	Per cent
P_2O_5	34.35
CaO	39.50
Na_2O	8.94
Fe_2O_3	11.25
F	0.07
SiO_2	3.51

Residue: various metal oxides present in the crude phosphate as impurities.

98.2 per cent of the phosphorus pentoxide are soluble in citric acid, 95.8 per cent are soluble in citrate.

(4.) 1 kilo of a mixture of equal parts of lime and clay is added to a mixture of 30 kilos of Pebble phosphate (32.5 per cent of P_2O_5, 47.6 per cent of CaO, 7.65 per cent of SiO_2, 3.7 per cent of F) with 5.7 kilos of sodium carbonate and 4.0 kilos of ferrophosphorus (containing 21.88 per cent of phosphorus and 4.81 per cent of silicon) and the whole is treated under the conditions indicated in Example 1. The product leaving the revolving furnace contains

	Per cent
P_2O_5	31.02
CaO	39.78
Na_2O	8.6
Fe_2O_3	10.61
F	0.08
SiO_2	6.85

Residue: various metal oxides present in the crude phosphate as impurities.

96.60 per cent of the phosphorus pentoxide are soluble in citric acid, 94.28 per cent are soluble in citrate.

(5.) A mixture of 25 kilograms of Morocco phosphate (34.5 per cent of P_2O_5, 49.6 per cent of CaO, 4.2 per cent of F, 3.75 per cent of SiO_2) with 4.75 kilograms of ferrophosphorus (containing 21.82 per cent of phosphorus and 3.36 per cent of silicon) and 38.6 kilograms of a spent lye containing 7.4 per cent by weight of Na_2O (in the

form of hydroxide, carbonate, formate, acetate) is treated under the same conditions as those described in Example 1, however, at a maximum temperature of the furnace of 1300° C. The product leaving the revolving furnace consists of

	Per cent
P_2O_5	33.39
CaO	38.40
Na_2O	7.52
Fe_2O_3	13.94
F	0.08
SiO_2	4.16

Residue: various metal oxides present in the crude phosphate as impurities.

95.6 per cent of the phosphorus pentoxide are soluble in citric acid, 94.7 per cent are soluble in citrate.

(6.) A mixture of 20 kilograms of Southern phosphate (32.20 per cent of P_2O_5, 45.32 per cent of CaO, 11.31 per cent of SiO_2, 3.12 per cent of F) with 2.40 kilograms of ferrophosphorus (containing 26.98 per cent of phosphorus), 3.36 kilograms of natural lime, (containing 47.6 per cent of CaO) and 3.16 kilograms of sodium hydroxide is treated as described in Example 1, however at a maximum temperature of the furnace of 1300° C. The roasted product contains

	Per cent
P_2O_5	31.32
CaO	42.25
Na_2O	7.90
Fe_2O_3	7.57
F	0.12
SiO_2	8.95

Residue: various metal oxides present in the crude phosphate as impurities.

94.6 per cent of the phosphorus pentoxide are soluble in citric acid, 92.7 per cent are soluble in citrate.

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