

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Fertilizers

I, JOHN CONRAD ARNOLD, of 10, Staple Inn, London, W.C.1., a British subject, do hereby declare the invention (a communication from Facerform Company, a Company duly registered under the laws of the State of New Jersey, United States of America, of 300, Pascack Road, Ridgewood, New Jersey, United States of America) for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to methods for the production of fertilizers containing phosphate having greater crop-producing capacity per unit of P_2O_5 than do conventional products, with or without additional fertilizer ingredients.

Superphosphatic fertilizers previously have been made by various methods in which the insoluble phosphates are converted by admixture with an acid to forms which are usable as food by plants. The most common method comprises mixing finely-ground phosphate rock with sulphuric acid to form a slurry, and then pouring the slurry into an enclosure called a den wherein a primary chemical reaction takes place without interruption and the mixture sets. At or near the conclusion of the primary chemical reaction, the freshly-reacted hot mass of nascent superphosphate is formed into discrete acidic particles. Thereafter during curing, a secondary chemical reaction takes place which is accompanied by great increase in heat, with accompanying loss of moisture. Storage for curing ordinarily is for an extended period of from several weeks to many months until chemical maturity reaches the point of commercial acceptability.

Numerous proposals have been made to modify the processing and cure to reduce the time and to improve the physical condition of the final superphosphatic product. However, no known proposals previous hereto have sought to improve the plant food value of the cured product, either qualitatively or, [Price 3s. 6d.]

to any substantial extent, quantitatively. In all previous proposals a substantial part of the water present after the digestive mass from the primary reaction is broken up is lost from the product during curing before it can be utilized in the crystallization necessary to secure and maintain the improved product which characterizes this invention.

This dehydration results from either the evaporation of water from the mass by exothermic reactions, associated with large amounts of heat, or because the mass is deliberately subjected to heat, or by auxiliary chemical reactions intentionally induced to evaporate water or to harden the mass, or by high pressure environments, suction, blasts of hot or cold air or steam, kneading the mass, or otherwise applying pressures.

Normally the curing is carried out simply by dumping the digestive mass, usually in the form of discrete particles, in large piles where it is left for a period of weeks or months. In such piles the mass coalesces into a huge monolith. The secondary and other reactions result in high heat. It is known to take steps to prevent such a great excess of heat that reversion to less soluble or completely insoluble forms of phosphorus is avoided or minimized, but in previous known processes it has not been recognised that even relatively moderate increase of heat and consequent loss of moisture from the material undergoing curing interfere with the securing and maintaining of maximum solubility (whether water-extractable or citrate soluble) and economy in use of acid. Moreover, in previous processes, such as pelleting, between the formation of the discrete particles and the piling for curing, moisture is often deliberately added and later withdrawn, generally by extraneous heat, thus preventing optimum crystallization.

This invention is based on the discovery that excessive heating resulting in the loss of water by evaporation and a deficiency in the total water necessary for crystallization after

the close of the primary reaction adversely affects the plant food value of the cured product, as well as its physical condition, and prevents the formation and preservation of the agronomically valuable anion which is characteristic hereof in the cured product. Later addition of water to compensate for such evaporation or deficiency does not avoid such damage. The term "dehydration" is applied generally to the foregoing conditions which in accordance with the present invention must be avoided.

The present invention provides a process for the manufacture of a fertilizer containing phosphate which comprises mixing an inorganic acid material and phosphate rock, the resulting product tending to set and develop heat, and after the digestive mass has hardened to such an extent as to be disintegrable without coalescing, breaking up the digestive mass, subsequent further hardening as well as curing of the broken-up mass taking place, thereafter curing said mass at normal pressures and obtaining a sensibly dry, free-flowing cured fertilizer product, wherein, from the time the mass is so broken up to the practical completion of curing (a) substantially no evaporation of the water content of the mass undergoing curing takes place and cooling goes on substantially continuously, and (b) the water content of the mass undergoing curing is such that the sensibly dry free-flowing cured fertilizer product which results from the process has been dried substantially entirely by crystallization alone.

By maintaining non-evaporative conditions from the time the mass is broken up to the practical completion of curing, substantially all the water present at the beginning of such period and necessary for optimum crystallization, is retained.

In the simplest form of the invention, no solids or liquids (apart from a finely-divided coating material which is used in small amounts when pellets are to be formed as later described) are added after the initial admixture of the phosphate rock and the inorganic acid material and, preferably, all the water that is required for the optimum crystallization is provided by the initial concentration of acid which concentration is substantially that which has heretofore been used in conventional processes of the type which involve mixing the ground phosphate rock and inorganic acid material, permitting the mixture to set in a den, disintegrating the set mass and subsequently curing the disintegrated mass by storage in large piles. Such a conventional concentration of the inorganic acid material when used in the process of the present invention, results in a sensibly dry, free-flowing cured product which has been dried substantially by crystallization alone and without the addition to or removal from the reaction mass of any substantial amount of water throughout the process.

In another form of the invention, additional fertilizer ingredients, particularly nitrogenous material and salts of potassium and other metals, may be added to the initial reaction mixture or to the digestive mass as it is being broken up, or immediately thereafter. The additional fertilizer ingredient may be added in finely-divided dry form or in liquid form, but in either case it may be necessary to make a slight adjustment in the initial water content of the disintegrated mass, preferably by a suitable adjustment of the initial acid concentration for the moisture absorbed by the fertilizer ingredient, if wet, or added therewith, if liquid, so that the water content of the mass undergoing curing is such that the product dries substantially entirely by crystallization alone.

The non-evaporative conditions of curing superphosphate herein described may advantageously be applied to a pelleted superphosphate fertilizer made in accordance with the process claimed in copending Application No. 27464/59 (Serial No. 828,882), a divisional application herefrom, and according to which small discrete particles of the product of the primary reaction between an inorganic acid material and phosphate rock, the surfaces of which are moist and acidic, are moved upon themselves while they are still moist and acidic from the primary reaction to form agglomerates approaching the size of the pellets desired and, while continuing said movement, the agglomerates are coated with an absorptive finely-divided material which forms a permanent thin layer thereon to physically complete the pellets, wherein, throughout the agglomeration and coating operations (a) all internal chemical reactions resulting from the acidity of the material are permitted to proceed unhindered by extraneous heating or neutralization and (b) the water content of the material being agglomerated and coated is such as to permit the interiors of the pellets to dry substantially entirely by crystallization alone, the foregoing steps alone serving to result in firm physically completed sensibly dry free-flowing pellets.

As the finely-divided coating material there may be used any material which under the conditions forms a continuous closed enveloping shell of appreciable thickness sufficient to physically support the pellet but it is preferred that the coating material is reactive with the surface acid of the agglomerates and is either itself a fertilizer ingredient, or is capable of yielding a fertilizer ingredient upon acidulation. Suitable finely-divided materials which may be mentioned are ground phosphate rock, ground dolomite, charcoal, bone black, bone char, lamp black, nitrogen-bearing organic materials including animal tankage and cottonseed meal, and potassic or phosphatic dusts.

For further details of the application of the process of this present invention to such a pelleted fertilizer, reference is directed to the

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specification of said copending application.

5 The inorganic acidic material which may be employed in the process of the present invention may be either sulphuric acid or phosphoric acid or a mixture of the two. As an alternative, however, to using liquid acid material, the process may be performed in accordance with the process claimed in a second copending Application No. 27936/59 (Serial No.), also a divisional application, herefrom, and according to which there is provided, a process for the manufacture of a fertilizer product in which a solid fertilizer raw material is reacted with an inorganic acid material characterised in that said raw material is acted with a preponderantly dry acidic sludge containing the inorganic acid material together with a fertilizer ingredient, said fertilizer ingredient, said fertilizer raw material and a material being such as to result in a dry fertilizer, the process being carried out in the absence of extraneously applied heat and without artificial drying of the product. The fertilizer ingredient may be any substance which is a fertilizer *per se* as opposed to a substance which is only made available for plant use upon acidulation. A particularly useful sludge which may be used according to this process is an ammoniated sludge formed by absorbing ammonia in sulphuric acid.

Other acidic sludges and further details of performing such a process are described in the specification of said second copending application, to which reference is directed.

35 The phosphate rock used in this invention is any raw phosphate or phosphatic ore and an important feature of the invention is that low grade phosphatic ores may be efficiently used which are too low in phosphate to be handled economically by any known process, if at all. Furthermore, this invention can be practised effectively with phosphate ores high in metal impurities, particularly iron and aluminium.

45 The presence of iron and/or aluminium, or other similar substances, in the phosphate rock which is to be acidulated has long presented serious problems both in known manufacturing operations and in their resulting products. In the presence of iron and aluminium known phosphate fertilizers quickly fix and become slowly if ever available for use by the plant. It has previously been held that rocks having more than from 3 to 5% of compounds of metals capable of forming sesquioxides, generally designated as R_2O_3 , if unable at all require excessive quantities of acid for acidulation and that in the finished product a portion of the available P_2O_5 reverts to unavailable. Moreover the resulting product has been sticky and gummy with free surface acid which rots bags. Therefore enormous quantities of such rocks are considered waste.

65 According hereto, however, rocks which are high in compounds of iron and/or aluminium and like metals can be acidulated with no

greater use of acid than required with ordinary phosphate rock and result in a product in which both the phosphorus and the metal are available for use by the plant. Therefore, according to this invention these phosphate rocks containing 5% R_2O_3 and even much more can be used with ease and economy and to supply an improved product.

In a product made hereby from an iron-containing rock, a ferrous phosphatic compound and a ferric phosphatic compound are produced both of which are in part truly water-soluble and in part soluble in the acidic solution which is created by their extraction in water.

If not already present in the phosphate rock, additional fertilizer ingredients containing iron or other metals may be added to the initial reaction mixture or to the digestive mass as it is being broken up or immediately thereafter. Metals which may be added in this way include:

Iron, which may be added as any iron salt which forms a soluble compound as previously stated, such as ferrous sulphate or as an ore which is economically acidulated.

Aluminium, though this element is so common in soils that it will rarely be added except in connection with special fertilizers for growing some ornamental plants.

Manganese, which may be added as manganese sulphate, a practicable source being rhodochrosite.

Zinc, from sources such as smithsonite and calamine.

Copper, which is an important additive, as copper sulphate, azurite or malachite. The importance of copper as an additive being that in this process it is converted to a water-soluble copper phosphate, whereas, normally, the addition of copper sulphate to a conventional superphosphate changes both copper and phosphorus into forms which cannot be used by a plant.

Magnesium, also of great importance particularly for sandy and highly acid soils, and usually added in the form of dolomite.

Other trace-elements which may be added include other alkaline earth metals such as barium and strontium, chromium, cobalt and nickel.

Further fertilizer ingredients additional to phosphorus which may be added include nitrogenous and potassic materials amongst which should be mentioned, ammonium sulphate, ammonium nitrate, urea, potash, potassium sulphate, potassium nitrate and potassium chloride.

A further advantage of the present invention is that the phosphate rock need not necessarily be ground to the degree of fineness customarily required by conventional processes thus saving both the time and expense of lengthy grinding operations.

The initial reaction of the phosphate rock

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- and the inorganic acid material may be performed in any convenient manner. In a practical and preferred method the ground phosphate rock is mixed with the inorganic acid material, with or without additional fertilizer material and this mixture of acidic material and ground rock is then handled either by the batch or continuous method. It may be placed in a widely used enclosure called a den, stationary or with a movable floor, wherein substantially all of the primary reaction takes place without interference or interruption. Dens used herein may be of many types, provided certain simple requirements are met. Formerly the most common type of den, still employed in many plants, was a brick or concrete enclosure into which the mixture was dumped and from which after the substantial completion of the primary reaction it was removed as by a bucket crane through a removable roof or by powered scoops or by mechanical excavating, cutting and disintegrating devices of many different kinds. In some instances, a disintegrator moves into the solidified mass and in others the mass is moved into a stationary cutter. Later, so-called automatic and continuous processes have been introduced, all of which include a den, although it often is not called by that name. Some have movable floors and others use a very slowly moving conveyor belt as a floor. All must be enclosed, in order to trap and remove various noxious gases. All of these devices, called by many different names, have the common purpose of receiving, or in some cases also forming, the mixture of rock and acid and furnishing facilities wherein the primary reaction proceeds to substantial completion in a substantially undisturbed state and then the reaction mass is made available for disintegration.
- After the digestive mass has set sufficiently to be disintegrable without coalescing, the digestive mass is broken up, again by quite conventional means, and optionally with the addition of further fertilizer ingredients during or immediately after disintegration. After the disintegration the particles may be agglomerated and coated according to the process of said first copending application, No. 27464/59 (Serial No. 828,882). The particles, or the pellets as the case may be, are then stored for curing under conditions effective to prevent loss of moisture until the practical completion of curing.
- The non-evaporative conditions required by the process of the invention may be achieved satisfactorily by storing the broken-up mass in a "ventilated pile." In such a method the freshly broken-up mass is placed in a storage space in a manner such that a large number of ventilating passages are provided through the mass sufficiently close together so that the heat of the secondary chemical reaction of the broken-up digestive mass is removed by convection without dehydrating the product. The disposition and diameter of the passages are chosen to carry off the heat at the optimum rate and to transmit it to the atmosphere before it can be absorbed. This arrangement from the time the digestive mass is broken-up until the practical completion of the curing thus avoids excessive heating and dehydration of the mass.
- In a practical method of forming such a ventilated pile the digestive mass is broken up into discrete particles, which are then placed in a storage space, which space is provided with a number of spaced vertical metal pipes about which the material is piled in relatively thin successive layers, each, say, of about one foot. When the material has further hardened sufficiently to hold its form the pipes may be moved upwardly, thus producing air passages leading in to the pile comprising passages formed in part by the material itself and in part by the pipes. As the pile is gradually built up, this process is repeated until the pile is complete, when the pipes may be removed. The material is then left in the receptacles undisturbed until the practical completion of curing. The actual length of time of curing depends upon the materials used and the formulation, but a maximum of about two weeks for practically complete cure and one week or slightly longer for safe removal may be taken as illustrative.
- Alternatively, particularly for new plants, the freshly broken-up digestive mass may be deposited about similar but fixed pipes installed in cars, which may be readily moved from the place where the discrete particles were formed to that of storage for curing.
- In descriptions of known processes there is much discussion of the avoidance of high heat during curing so that retrogradation of water-extractable (miscalled water-soluble) phosphate or available phosphate does not take place. Many expedients to overcome this evil have been proposed. One plan commonly used in older batch plants making use of cranes to excavate dens has been to pick up the super-phosphatic material after it has been stored in large curing spaces, carry it to another spot and then drop it, this operation tending to cool the mass. Thereupon when the temperature has again reached a point close to that at which retrogradation is feared the process has been repeated. This invention is not concerned with retrogradation. According to the practice hereof the temperature of the mass being cooled must be held at a much lower level than that which will cause retrogradation. Otherwise the particular chemical results of this invention will not be obtained. Procedures which are successful in avoiding retrogradation would be completely useless herein because the damage already would have taken place. No exact temperature limits can be given because the requirements of products made from different types of phosphate rock and of different end

concentrations are different. Merely for the purposes of illustration it can be said that a water solution of the product hereof loses its characteristic properties, to be described later, and becomes the same as that of known products when heated to approximately 160° F. Mixtures of some phosphate rocks and acidic material while being cured will tolerate somewhat higher heat in the curing pile than this figure but not that common in conventionally known processes.

A characteristic of the process of the invention which is achieved by piling the broken-up mass in a "ventilated pile" is that substantially all the exothermic heat of the secondary reaction after the digestive mass is broken up is transmitted substantially directly to the atmosphere and not absorbed by the broken-up mass. Preferably the exothermic heat is transmitted to the atmosphere at a rate such that the temperature of the broken-up mass decreases substantially continuously until the practical completion of curing.

The processes of the present invention provide for the curing of the broken-up mass, including the pelleted product, in a greatly shortened period of time and at substantial savings in cost for plant, materials, equipment and labour and simultaneously improve both the plant food value, including the degree of conversion of the insoluble phosphate of the rock per unit of acidic potential applied thereto, and the physical properties of the cured product.

The cured product contains a novel truly water-soluble acidic anion, later described, which results in increased crop growth per unit of P_2O_5 , and originally has and maintains an unusually high water-extractability of its phosphatic components per unit of acid applied to the phosphate rock. Further increased water-extractability is secured and maintained without over-acidulation of the rock and, highly important, with the use of a lower ratio of

acidic potential to available phosphate than commonly achieved in an economic production operation for a cured product.

The advantages achieved by the process of the present invention such as saving of rock and/or acid, will be clear from the following comparison of two samples of a fertilized product prepared and cured in accordance with the principles of the present invention and two samples of a fertilizer product prepared and cured by conventional methods.

Sample I is a superphosphate prepared according to the invention and analyses as follows:

Moisture at 100° C.	5.60%
Total Phosphoric Acid	20.90%
Insoluble Phosphoric Acid	.06%
Available Phosphoric Acid	20.84%
Water-extractable Phosphoric Acid	19.13%

Sample II is a superphosphate similar to Sample I but agglomerated and coated with 100 pounds of rock dust in accordance with the process of said first copending application No. 27464/59 (Serial No. 828,882) and analyses as follows:

Moisture at 100° C.	4.50%
Total Phosphoric Acid	21.05%
Insoluble Phosphoric Acid	.90%
Available Phosphoric Acid	20.15%
Water-extractable Phosphoric Acid	18.30%

Sample III is a superphosphate prepared and cured in a conventional method.

Sample IV is a pelleted superphosphate prepared by "nodulizing" 12 days after mixing a conventional superphosphate by tumbling wet in a rotary drum and then dried. The analysis being made 12 days after nodulizing.

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TABLE

	Sample I	Sample II	Sample III	Sample IV
Phosphate rock (lbs)	1150	1250	672	1125
Percent P_2O_5	33	33	31.3	33.4
Total P_2O_5 (lbs)	379.5	412.5	210.3	375.7
Sulphuric Acid (lbs) } At 60° B	850	850	525	960
P_2O_5 made available (lbs)	378.4	394.8	190.5	368.4
P_2O_5 made available percent of total	99.7	95.7	90.6	95.4
P_2O_5 insoluble percent of total	0.3	4.3	9.4	4.6
lbs. Rock per lb. Acid 60° B	1.35	1.47	1.27	1.17
lbs. Rock per lb. available P_2O_5	3.039	3.166	3.522	3.053
lbs. 60° Acid per lb. available P_2O_5	2.26	2.15	2.76	2.605



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5 A comparison of Samples I and III shows that for an unpelleted fertilizer, there is a saving in both acid and rock per pound of available P_2O_5 produced. A comparison of Samples II and IV shows, for a pelleted fertilizer, a saving in acid. From such saving in rock and/or acid other advantages such as saving in cost and labour automatically follow.

9 The cured products of the invention, including the pelleted product, possess and maintain an unusually high water-extractability of their phosphatic components in relation to acidic and other materials employed. Water-extractability is to be distinguished from water-solubility. Water-solubility refers to the dissolution of a substance in water to form a solution in which the concentration of each element in the solution is the same as that of the same element in the undissolved solid. Water-extractability refers to the disappearance in water of certain or all of the parts of the substance whether the resulting water-extract is a pure solution of the original solute or not. Thus water-extractability can exist without water-solubility.

30 The water-extractable phosphatic product of the invention contains a truly-water-soluble component which has much greater crop-producing capacity than conventional phosphate fertilizers which are merely water-extractable. Such water-extractable phosphate

fertilizers are decomposed in the presence of water and the products of such decomposition are such as to combine with basic elements in the soil to form chemically-stable compounds which resist the digestive action of growing plants. In contrast, the characteristic water-soluble anion hereof, upon combination with such substances, produces truly water-soluble substances easily utilized as food by growing plants. The products of the invention when subjected to soil-water yield substances in which the hydrogen atoms remain in true combination with phosphorus so that change to a compound which is indigestible by the plant is either avoided or long delayed.

While the fertilizer industry assumes that superphosphate comprises monocalcium phosphate, dicalcium phosphate and tricalcium phosphate, and that monocalcium phosphate is "soluble in water," dicalcium phosphate is "insoluble in water" but "soluble in weak acid" and "tricalcium phosphate" is, practically speaking, "insoluble," it should be noted that, in fact, monocalcium phosphate is not truly water-soluble except to a negligible degree, but is merely water-extractable. The water-extract of calcium monophosphate contains dissolution products which are susceptible to combination with other molecules or radicals which may be present in the extract or the soil and in many cases such combinations are unavailable for plant use.

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Only a small portion of the phosphorus in known fertilizers which is applied to the soil is actually utilized by the plant, although a large portion of the nitrogen and potash so applied is utilized. Experiments have shown that the plant ordinarily secures only between 10 and 20% of all phosphorus from good commercial fertilizers.

Field tests of the product of this invention indicate that per unit of phosphorus applied increases in plant growth run from 10 to 300% over the present utilization of from 10 to 20% of the total so-called "available" phosphorus applied.

The characteristic product hereof is particularly well adapted to the following usual types of soils:

1. Acid soils which lack phosphorus usable by the plant but have certain metals, notably iron and aluminum, often in excess, in forms usable by the plant.

Also, in slightly acid soil (pH of about 6.0 to 6.8) both the minor metallic elements and phosphorus in plant-available forms in quantities to produce maximum growth are lacking.

2. Soils which are generally sandy and are adapted for specialized agricultural use but often considered marginal without improvement may have an abundance of phosphorus but lack minor elements, e.g. magnesium.

3. Highly alkaline soils may be of no practical agricultural importance, but those of a pH value of 8, or higher, have sufficient phosphorus in a form which cannot be used by a plant because of lack of hydrogen, with calcium and other metals also unavailable.

The superphosphatic fertilizer hereof meets the difficulties of all such soils. The preferred product hereof includes an acidic phosphate salt (having H atoms) which is truly water-soluble which ionizes in solution and in the presence of metallic compounds which are soluble and react to produce acidic phosphates of these metals. One aspect of the invention, therefore, is the production and maintenance of a truly acidic soluble phosphorus salt which maintains its hydrogen atom within the radical within the fertilizer complex and its H ion in association with the radical when the material goes into solution within the soil so that other acidic salts are formed which resist fixation. This characteristic is particularly valuable when this product is applied to soils high in the metals. In such soils, wherein water-extractable phosphates quickly fix, as do citrate-soluble unless promptly digested and assimilated by plants, this truly water-soluble acidic salt tends to form other metallic phosphatic salts which are truly water-soluble in turn. This factor appears to be among those which account for the increased crop growth of the product of this invention.

The product herein produced, as shown by titration with a normal base solution, has a

total acid content comparable to the mean acid content of conventional materials. Although the free acid content of the product of the present invention is not substantially greater than that of conventional superphosphate, it does have instantly available in all dilutions a relatively greater quantity of H ions. This characteristic makes possible the conditions favorable to the formation of soluble phosphatic salts without the presence of an actual excess of acid.

In order to illustrate more fully this invention and its comparison with known superphosphates over which it improves, reference is made to the drawings, of which:

Figures 1 to 8 are reproductions of photomicrographs each enlarged approximately 125 diameters of crystals formed from water-extracts of the various substances hereinbelow treated with the substances specified;

Fig. 1: The product of the invention treated with hexamine cobaltic chloride;

Fig. 2: A standard mixture of monocalcium phosphate and calcium hypophosphite with hexamine cobaltic chloride;

Fig. 3: A standard mixture of conventional superphosphate with hexamine cobaltic chloride;

Fig. 4: A standard mixture of monocalcium phosphate, dicalcium phosphate and calcium pyrophosphate with hexamine cobaltic chloride;

Fig. 5: The product of the invention with ammonium chloride;

Fig. 6: A standard mixture of monocalcium phosphate and calcium hypophosphite with ammonium chloride;

Fig. 7: Conventional superphosphate with ammonium chloride;

Fig. 8: A standard mixture of monocalcium phosphate dicalcium phosphate and calcium pyrophosphate treated with ammonium chloride.

The products hereof are best compared to those of the prior art by crystallography. Ordinarily inorganic chemical analysis is based upon reducing the constituents of an unknown compound to their elementary condition or of converting them into some standard substance which can then be measured. Such analysis, however, does not meet a situation in which the result is to be stated not in terms of the elementary composition of a compound but of the characteristic ions present in the water-extract *before* analysis. This problem now has been solved by the separation of a compound into its significant constituents or ions which may be either elementary or as in this case a radical. Thus while the identification of elements which are present does not necessarily identify the original material, the identification of significant ions is by a study of the specific crystalline formation which is peculiar to various compounds. Analyses of crystals formed from water-extracts of the product of this invention and of typical conventional superphos-

phate were made. These findings were then employed as bases for the preparation of corroborative standards from chemically pure materials. According to this technique, the crystals which are being described and illustrated as standards are not crystals of the product according to the invention or of known products but of a laboratory solution or a laboratory solution treated with a specific and named reagent.

The characteristic chemical composition of the fertilizer according to the present invention is destroyed when the material is heated to above 160° F. and the fertilizer of the invention then chemically reverts to a material equivalent to conventional superphosphate.

The crystals illustrated in the figures as indicated below were made from water-extracts of the following substances:

1. Superphosphate prepared according to this invention.

2. A standard comprising calcium hypophosphite and monocalcium orthophosphate in the ratio of 2 parts to 5.

3. A conventional superphosphate.

4. A standard comprising a filtered aqueous extract of a mixture of eight parts of monocalcium phosphate, one part of calcium pyrophosphate and one part of dicalcium phosphate, each chemically pure.

Analyses of superphosphate according to the invention indicates the presence therein of monocalcium phosphate in association with a product which responds to tests for calcium hypophosphite. Analyses of several conventional superphosphates showed calcium pyrophosphate and dicalcium phosphate as constituents in addition to monocalcium phosphate. Therefore these two materials were used in making the comparison standard against which the conventional superphosphate was checked.

Each standard extract was given an acid reaction similar to the corresponding water-extract of the superphosphates and thereupon treated with the two following recognized micro-reagents:

1. Hexamine cobaltic chloride.

2. Ammonium chloride.

Figure 1 shows a crystal formation of a water-extract of the superphosphate of this invention treated by hexamine cobaltic chloride. The base of the field is made up of comparatively anisotropic colorless fusiform crystals, singly, in pairs, radiates and sheaves. Interspersed are typical deformed hexagonal crystals of a distinct yellow. These crystals are anisotropic and with low birefringence and are secondary and tertiary developments of hexagonal rosettes. The colorless crystals when grouped in sheaves and larger aggregates are so highly refractive that they scatter light outside the microscopic field giving them the appearance of dull opaque solids of irregular shape.

Figure 2 illustrates a standard made of a

mixture of monocalcium phosphate and calcium hypophosphite treated by hexamine cobaltic chloride. The form of this crystal is less complex than that of Figure 1 but exhibits the same fundamental characteristics but in two different stages of the identical crystal habit. The fusiform of the background are not developed to the same degree as those of Figure 1 since they remain largely single, double and simple radiates. The yellow hexagonal rosettes display their fundamental form more distinctly than do those of Figure 1.

Figure 3 illustrates a formation made of a mixture of known superphosphate treated with hexamine cobaltic chloride. The background is made up of minute granular crystals which gradually increase in size until they form the roughly trigonal center around which the typical crystal is built. It starts with a trigonal form which develops asymmetrically into an irregular leaf-shaped crystal with 3, 4 or 5 major limbs, hardly any forms suggesting a hexagonal symmetry. As these crystals increase in size one arm develops considerably at the expense of the others and near one end 2 arms at 90 degrees and almost equal in size are found. A very short arm which appears to be a continuation of the long arm completes the definite cross or dagger-shape of this typical crystal. Neither in background nor principle does this material resemble that of specimens shown in Figures 1 and 2.

Figure 4 illustrates a standard formed by said mixture of monocalcium and pyrophosphate and dicalcium phosphate treated by hexamine cobaltic chloride. This preparation is characterized by irregular leaf-shaped crystals and also isometric leaf forms similar to those found in Figure 3 as well as a similar birefringence. The typical crystal of this group, however, is a dagger-shaped crystal which is much more highly developed than the crystals of Figure 3.

The four specimens illustrated in Figure 1 to 4 treated with hexamine cobaltic chloride divide sharply into two groups of two substances. The standard formed from a mixture of monocalcium orthophosphate and calcium hypophosphite exhibits characteristics similar to those of the herein produced product, while there is an unmistakable relation between mixtures of monocalcium and dicalcium orthophosphate and pyrophosphate and that of conventional superphosphate.

In the next set of specimens, namely those shown by Figures 5—8, crystals from the same water-extracts as in the foregoing group were treated with ammonium chloride.

Figure 5 shows a crystal formation of the characteristic superphosphate made by the process of the present invention treated by ammonium chloride. The entire specimen exhibits small fusiform crystals, which except for grouping in clusters have definite and uniform appearance, in singles, doubles, simple





radiates, and clusters. The individual crystals are laminate and anisotropic. The clusters are so refractive that by non-polarized light they appear to be opaque rough and of irregular shape but under polarized light are seen to be complex aggregates of the crystal which characterizes the body of the specimen.

Figure 6 is a standard composed of a crystal formation of a combination of monocalcium phosphate and calcium hypophosphite of a ratio of the order of 2 to 5 treated with ammonium chloride. This material exhibits the highly refractile rough crystal of the reagent interspersed with translucent opaque clumps which upon examination with polarized light are shown to be clusters of anisotropic crystals. These crystals are more definitely rhomboid than the fusiform crystal of Figure 5 and the individual crystals are considerably smaller. Both of these conditions, however, indicate merely alternate habits of the same material inasmuch as their crystallographic identity and habit of grouping are the same and the scattering of minute single and double crystals about the clusters is common to both.

Figure 7 illustrates a distinctive crystal formation of conventional superphosphate treated with ammonium chloride. Upon a background of square plates is superimposed the typical ladder crystal which consists of broad irregularly swollen limbs with primary, secondary and tertiary branches all leaving the parent stem substantially at right angles although there may be deviations of 10 or 15 degrees. This crystal is isotropic. Entwined with it is a segmented linear crystal growth which branches at acute angles which is strongly anisotropic.

Figure 8 illustrates a standard formed of said mixture of monocalcium and dicalcium phosphate and pyrophosphate treated by ammonium chloride. This preparation exhibits the typical square branch habit of the crystal of Figure 7 and is identical except that it lacks the characteristic rectangular background crystals of Figure 7. Since differences in size and formation are characteristic of temperature and humidity of the evaporating atmosphere and the concentration of the solution they have no bearing upon identity.

The marked similarity between Figures 5 and 6 in one case and between 7 and 8 in the other is unmistakable. This similarity, confirming the results obtained with the other reagent, emphasizes the close chemical relation existing between the average conventional superphosphate and a mixture of pyrophosphate and orthophosphate.

It will be understood that the above crystallographic descriptions of the product hereof identify a superphosphate fertilizer only when made without the addition of other fertilizer materials. Such addition would entirely change the appearance of the crystals. Also the addition of even small quantities of other forms

of phosphorus, as for example a metaphosphate or a pyrophosphate, will produce a different crystal. Nevertheless, crystals of such mixtures when treated with appropriate reagents illustrate the same differences with phosphatic components themselves.

The superiority of the product of the present invention may be considered to be due either to calcium hypophosphite or a polymerized phosphatic salt which is water-soluble and contains one or more replaceable hydrogen atoms and in other ways reacts in a manner similar to calcium hypophosphite. It is probable that either hypophosphite or a similar acting and at present unknown phosphatic salt acts in association with monophosphate, this association perhaps being a physical mixture but more likely being that of a double salt.

For all practical purposes of identification one may define the characteristic element of the product herein produced as a persistent acidic salt with one or more replaceable hydrogen atoms embodying the characteristics of hypophosphite in association with monophosphate. Whether this substance is actually hypophosphite or another acid salt such as a polymer which has the same characteristics is unimportant.

The product hereof contains a characteristic substance, which is herein called "hypophosphite," which tends to render the entire complex truly water-soluble, generally but not always up to the measure of the water-extractability of the compound. This is to say, while probably slightly less than $\frac{1}{2}$ of a water-extract of this product comes from this hypophosphite as defined above and is recognized as water-soluble, the presence of that substance renders the remainder water-extractable phosphatic complex truly water-soluble in whole or in part.

An important characteristic of the product hereof is the presence therein of water-soluble calcium to an amount materially greater than that for which water-soluble calcium phosphate can be responsible. Water-soluble sulphur is also present in an amount indicating that both calcium and sulphur come from water-soluble calcium sulphate. These amounts materially exceed $1\frac{1}{2}$ to 2% of the calcium sulphate present, which is the largest amount in any conventional product.

Many soils are deficient in calcium in a utilizable form. Calcium greatly assists in rendering other plant foods usable. Sulphur, also, is necessary in certain soils. Water-soluble calcium and sulphur in combination do not change the acid-alkaline balance of the soil.

In all the processes hereof without any change in principle phosphoric acid may be substituted for all or part of the sulphuric acid to produce enriched or triple superphosphate. The phosphate content of the superphosphate products thus available by the process of the invention range from normal (say 16 to 20%.

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P_2O_5), to enriched (say 20 to 42% P_2O_5) or to triple (say 42 to 50% P_2O_5). Enriched superphosphate may, however, contain no more than 16 to 20% P_2O_5 if it is made from phosphate rock so low in phosphate that by known processes a physically and economically satisfactory product is impossible.

The following example illustrates the process of the invention as applied to the production of a normal superphosphate.

EXAMPLE.

A normal simple superphosphate is prepared by the method of the ventilated pile from the following components:

850 lbs. sulphuric acid calculated at 60° B., at 60° F. and used at from 52° to 56° B.; and

1150 lbs. ground Florida pebble rock or its equivalent of 68 to 75 % bone phosphate of lime.

The concentration of the acid is determined as if the process were conventional, in accordance with the characteristics of the particular rock used, and other usual variants. Different grades and types of rock will require slight adjustment of the ratio of rock to acid. Note, however, that according to this process, each pound of sulphuric acid calculated at 60° B. produces 2.25 lbs. of available P_2O_5 . The ground phosphate rock is mixed with the acid and the mixture placed in a conventional den to set. When the mixture has set sufficiently to be disintegrable without coalescing the mixture is excavated from the den and disintegrated.

After disintegration, the broken-up mass is placed in a storage space provided with ventilating pipes of ordinary metal of 6" to 12" in diameter and spaced within about 4 feet of each other and provided with means for raising and lowering them.

The broken-up mass is placed in the storage space in successive layers of about one foot in thickness. As the material is piled up and has further hardened sufficiently to hold its own form, the metal pipes are gradually raised and eventually removed from the complete pile leaving behind ventilating passages extending right to the base of the pile.

In the pile thus formed no part of the nascent superphosphate is more than about 3 feet from one of the ventilation passages.

The nascent superphosphate is then left until the practical completion of curing, from one to two weeks, when the fertilizer product may be removed from the pile and bagged or otherwise stored ready for use in the form of a sensibly dry free-flowing cured product.

WHAT I CLAIM IS:—

1. A process for the manufacture of a fertilizer containing phosphate which comprises mixing an inorganic acid material and phosphate rock, the resulting product tending to set and develop heat, and after the digestive mass has hardened to such an extent as to be

disintegrable without coalescing, breaking up the digestive mass, subsequent further hardening as well as curing of the broken-up mass taking place, thereafter curing said mass at normal pressure, and obtaining a sensibly dry, free-flowing, cured fertilizer product wherein, from the time the mass is so broken up to the practical completion of curing, (a) substantially no evaporation of the water content of the mass undergoing curing takes place and cooling goes on substantially continuously, and (b) the water content of the mass undergoing curing is such that the sensibly dry free-flowing cured fertilizer product which results from the process has been dried substantially entirely by crystallization alone.

2. A process according to Claim 1, in which the acid material is sulphuric or phosphoric acid or a mixture of the two.

3. A process according to Claim 1 or 2, in which the initial concentration of acid material is such that there results a sensibly dry, free-flowing cured product which has been dried substantially entirely by crystallization alone and without the addition or removal of any substantial amount of water from the reaction mass throughout the process.

4. A process according to any one of the preceding claims, in which the broken-up mass subsequent to the breaking up is promptly heaped in piles, which piles are provided with ventilation passages extending thereinto such that the exothermic heat of the broken up mass is transmitted substantially directly to the atmosphere, the temperature of the broken-up mass decreasing substantially continuously from the moment of piling to the practical completion of curing.

5. A process according to Claim 4, in which the broken-up mass is piled about vertical metal pipes, which pipes constitute the ventilating passages extending into the pile.

6. A process according to Claim 5, in which the broken-up mass is piled about said metal pipes in successive relatively thin layers and in which, as the pile is built up and as the broken-up material in the pile further hardens sufficiently to hold its form, said pipes are gradually raised until at the completion of the pile the walls of the ventilating passages are formed in part by the material of the broken-up mass itself and in part by the pipe.

7. A process according to Claim 6, except that the pipes are eventually removed from the pile, the walls of the ventilating passages thus being formed entirely by the material of the broken-up mass itself.

8. A process according to any one of the preceding claims, in which an additional fertilizer material is added to the initial reaction mixture or to the digestive mass as it is being broken up or immediately thereafter.

9. A process according to Claim 8, in which the additional fertilizer ingredient contains a salt of a metal other than calcium.

5 P_2O_5), to enriched (say 20 to 42% P_2O_5) or to triple (say 42 to 50% P_2O_5). Enriched superphosphate may, however, contain no more than 16 to 20% P_2O_5 if it is made from phosphate rock so low in phosphate that by known processes a physically and economically satisfactory product is impossible.

10 The following example illustrates the process of the invention as applied to the production of a normal superphosphate.

EXAMPLE.

A normal simple superphosphate is prepared by the method of the ventilated pile from the following components:

15 850 lbs. sulphuric acid calculated at 60° B., at 60° F. and used at from 52° to 56° B.; and

20 1150 lbs. ground Florida pebble rock or its equivalent of 68 to 75 % bone phosphate of lime.

The concentration of the acid is determined as if the process were conventional, in accordance with the characteristics of the particular rock used, and other usual variants. Different grades and types of rock will require slight adjustment of the ratio of rock to acid. Note, however, that according to this process, each pound of sulphuric acid calculated at 60° B. produces 2.25 lbs. of available P_2O_5 . The ground phosphate rock is mixed with the acid and the mixture placed in a conventional den to set. When the mixture has set sufficiently to be disintegrable without coalescing the mixture is excavated from the den and disintegrated.

35 After disintegration, the broken-up mass is placed in a storage space provided with ventilating pipes of ordinary metal of 6" to 12" in diameter and spaced within about 4 feet of each other and provided with means for raising and lowering them.

40 The broken-up mass is placed in the storage space in successive layers of about one foot in thickness. As the material is piled up and has further hardened sufficiently to hold its own form, the metal pipes are gradually raised and eventually removed from the complete pile leaving behind ventilating passages extending right to the base of the pile.

50 In the pile thus formed no part of the nascent superphosphate is more than about 3 feet from one of the ventilation passages.

55 The nascent superphosphate is then left until the practical completion of curing, from one to two weeks, when the fertilizer product may be removed from the pile and bagged or otherwise stored ready for use in the form of a sensibly dry free-flowing cured product.

WHAT I CLAIM IS:—

60 1. A process for the manufacture of a fertilizer containing phosphate which comprises mixing an inorganic acid material and phosphate rock, the resulting product tending to set and develop heat, and after the digestive mass has hardened to such an extent as to be

disintegrable without coalescing, breaking up the digestive mass, subsequent further hardening as well as curing of the broken-up mass taking place, thereafter curing said mass at normal pressure, and obtaining a sensibly dry, free-flowing, cured fertilizer product wherein, from the time the mass is so broken up to the practical completion of curing, (a) substantially no evaporation of the water content of the mass undergoing curing takes place and cooling goes on substantially continuously, and (b) the water content of the mass undergoing curing is such that the sensibly dry free-flowing cured fertilizer product which results from the process has been dried substantially entirely by crystallization alone.

2. A process according to Claim 1, in which the acid material is sulphuric or phosphoric acid or a mixture of the two.

3. A process according to Claim 1 or 2, in which the initial concentration of acid material is such that there results a sensibly dry, free-flowing cured product which has been dried substantially entirely by crystallization alone and without the addition or removal of any substantial amount of water from the reaction mass throughout the process.

4. A process according to any one of the preceding claims, in which the broken-up mass subsequent to the breaking up is promptly heaped in piles, which piles are provided with ventilation passages extending therein to such that the exothermic heat of the broken up mass is transmitted substantially directly to the atmosphere, the temperature of the broken-up mass decreasing substantially continuously from the moment of piling to the practical completion of curing.

5. A process according to Claim 4, in which the broken-up mass is piled about vertical metal pipes, which pipes constitute the ventilating passages extending into the pile.

6. A process according to Claim 5, in which the broken-up mass is piled about said metal pipes in successive relatively thin layers and in which, as the pile is built up and as the broken-up material in the pile further hardens sufficiently to hold its form, said pipes are gradually raised until at the completion of the pile the walls of the ventilating passages are formed in part by the material of the broken-up mass itself and in part by the pipe.

7. A process according to Claim 6, except that the pipes are eventually removed from the pile, the walls of the ventilating passages thus being formed entirely by the material of the broken-up mass itself.

8. A process according to any one of the preceding claims, in which an additional fertilizer material is added to the initial reaction mixture or to the digestive mass as it is being broken up or immediately thereafter.

9. A process according to Claim 8, in which the additional fertilizer ingredient contains a salt of a metal other than calcium.



10. A process according to Claim 9, in which the fertilizer ingredient contains a salt of one or more of the metals aluminium, copper, iron, magnesium and zinc.
- 5 11. A process according to Claim 1, wherein the phosphate rock contains compounds of metals capable of forming sesquioxides of more than 5% by weight of the rock and the ratio of the acidic material to the phosphate in the rock is not more than stoichiometric.
- 10 12. A process according to Claim 1, wherein the inorganic acid material is a preponderantly dry acidic sludge containing an inorganic acid material together with a fertilizer ingredient.
- 15 13. A process according to Claim 12, wherein the acidic sludge is an ammoniated sludge formed by absorbing ammonia in sulphuric acid.
- 20 14. A superphosphatic fertilizer produced by the process of Claim 1, including a calcium salt of an oxygenated acid of phosphorus, said fertilizer in contact with water yielding an aqueous extract which responds to tests for hypophosphite.
- 25 15. A fertilizer produced by the process of Claim 1, containing a water-soluble phosphorus anion which in aqueous solution in the presence of soluble calcium reacts crystallographically in the manner of an aqueous solution of a mixture of calcium hypophosphite and chemically pure calcium monophosphate.
- 30 16. A fertilizer produced by the process of Claim 1, which in contact with water yields an aqueous extract which reacts crystallographically in the manner of an aqueous solution containing calcium hypophosphite and chemically pure calcium monophosphate in the ratio of 2 parts to 5.
- 35 17. A superphosphatic fertilizer produced by the process of Claim 1, which when not heated above 160° F. contains a phosphatic component of which a water-extract when treated by hexamine cobaltic chloride includes a microscopic field made up of comparatively anisotropic fusiform colourless crystals through which are interspersed deformed yellow hexagonal anisotropic crystals with low birefringence, these hexagonal rosettes being secondary and tertiary developments of hexagonal rosettes.
- 40 18. A superphosphatic fertilizer produced by the process of Claim 1, which when not heated above 160° F. contains a phosphatic component of which a water-extract when treated by ammonium chloride exhibits microscopically small fusiform anisotropic and laminate crystals forming the body of the specimen and except for grouping in clusters have definite and uniform appearance in singles, doubles and simple radiates, the clusters being so refractive that by plane light they appear to be opaque, rough and irregular shape but by polarized light are shown as combined aggregates of the crystal formation which characterizes the body of the specimen.
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