

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Production of Fertilizers

5 I, CHARLES HENRY JOURDAN, of "Gracefield," Lacey Green, near Princes Risborough, Buckinghamshire, a British subject, [the personal representative of JOHN CONRAD ARNOLD deceased, late of 9 Staple Inn, London, who has hereby declared in writing, (a communication from Fairform 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:—

15 This invention relates to the manufacture of pelleted fertilizers containing phosphate and, optionally, other fertilizer ingredients.

20 Pelleted and granular superphosphate fertilizers have been formed by many processes. All of these known processes depend upon principles and procedures which are not used in this invention and if so used would defeat its purpose. To form agglomerates the great majority use water in excess of that necessary for chemical purposes. They process the digestive or digested mass as a slurry and later remove excess water, for example, by external heat, vacua, or air blasts, or chemically produced exothermic heat from the reaction of added acids or bases, particularly ammonia.

30 Many processes of this type pass the fertilizer material to be pelleted through one or more "conditioners" wherein agglomerates are formed, generally with the addition of water, generally as such, occasionally as blasts of steam and often in the form of a dilute or other acid. Thereafter, no matter what the details of the respective processes, the pellets must be dried by external means, then generally cooled in another separate and expensive operation, and then cured for much longer periods than is necessary herein. Generally these processes start with fine superphosphate

45 which has been completely processed and cured, or they may introduce partially or

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wholly cured phosphatic material or other dry material into the mass being processed because of its cooling or solidifying effect. Whatever process is used, however, the removal of this excess water also removes some of the water necessary to the chemical reactions still proceeding within the pellets and also, in some cases, reversion of the reacted phosphatic material occurs.

50 Numerous proposals have been made to produce pellets by extrusion. A digestion mass of phosphate rock and acid may be placed under substantial pressure. With or without added plant food materials and with or without the addition of more water, the mass is forced through an apertured plate, the resulting cylinders cut off, and, after short preliminary curing, stored for complete cure. The water content of the extruded mass is critical.

55 Another known process in the production of superphosphates or compound fertilizers passes a slurry of acid and raw phosphate rock from a first mixer into a second mixer wherein is added a portion of the material which has already undergone reaction and is partially or completely dried. Both are true mixing operations carried out while the primary reaction is still progressing and in blasts of cool or hot air. Similarly, cured or largely cured superphosphate is made into a flowable slurry which then passes to a conditioner wherein fertilizer salts are later added with water or ammoniacal liquid, causing heat, and then to a second conditioner wherein the moisture content is controlled by the addition of moisture-absorbing off-sized processed material. Nevertheless, thereafter in both instances the pellets must be artificially dried, and cured.

60 It also has been proposed to produce under conditions of continuous forced cooling a granular calcium nitrate and phosphate by making a fluid mixture of nitric acid and conventional cured normal superphosphate, and also phosphate rock and sulphuric acid, with or without other plant foods. A fluid mixture is obtained comprising phosphoric acid and

calcium nitrate. An essential characteristic is the introduction of a considerable portion of the finished product as a coolant and also as a seeding agency. The product may be solidified by being spread in a thin layer and suddenly cooled to -12°C .

In all known pelleting processes, including those known as granulating, the product is sized after completion, generally with at least 50% of the pellets oversized or under-sized. In many instances this off-size material is necessary for return to the circuit as an essential part of the operation. In some processes the off-sized material being re-circulated is as much as twenty times the output. In any case this re-sizing is expensive and adds complications. Many of these known processes produce only granules and are unable to make what herein are called pellets of a size larger than mere granules, which are scarcely larger than individual grains of well-made fine superphosphate.

In contrast to the foregoing processes, a fundamental characteristic of the present invention is that the agglomerating operation of the product of the primary reaction between an inorganic acid material and a phosphate rock is performed not with a slurry from which excess water is removed nor upon dry material to which water is added but upon preponderantly solid but moist particles and in the absence of any extraneous heat tending to remove moisture and in the absence of any neutralizing agent tending to interfere with the chemical reactions proceeding within the agglomerates, the pellets being physically completed by coating the agglomerates, while still moist, with a dry finely divided absorptive material which adheres to the surface of the agglomerates and presents a substantially dry exterior.

By "extraneous heat" is meant any artificially applied heat, whether physically or chemically produced, which is applied for the purpose of removing moisture from the material being agglomerated and coated. The chemical reactions occurring within the material being agglomerated and coated and subsequently during curing are exothermic and therefore some heating occurs, but during agglomeration and coating such heat is dissipated so quickly as to result in only negligible loss of moisture by evaporation. For full agronomic benefit from this invention, special conditions are also applied to the physically completed pellets during curing, such preferred conditions being described more fully herein-after and resulting in substantially no loss of moisture from the pellets until the practical completion of curing. However, the benefits from the process of the invention even without the application of such special conditions, are so great that in practice such special conditions will usually be dispensed with.

In accordance with the broad aspect of the

present invention, there is provided a process for the manufacture of a pelleted fertilizer containing phosphate which comprises providing small discrete particles of the product of the primary reaction between an inorganic acid material and phosphate rock, the surfaces of which particles are moist and acidic, moving the discrete particles 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, coating the agglomerates with 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.

Preferably the process is carried out without the addition to or removal from the material being processed of any substantial amount of water throughout the entire process, the initial concentration of the inorganic acid material being such that there result firm physically completed sensibly dry free-flowing pellets, the interiors of which have dried substantially entirely by crystallization alone.

Optionally, a fertilizer ingredient additional to phosphorus may be added to the material being processed before or during agglomeration and before coating. The additional fertilizer ingredient may be added in finely-divided dry form in which case it may be necessary for the purposes of agglomeration to make allowance, preferably by suitable adjustment of the initial acid concentration, for the relative decrease in moisture content of the material being processed. Alternatively, the additional fertilizer ingredient may be added in moist or liquid form in which case it may similarly be necessary to make allowance for the increase in the water content of the material.

The absorptive finely divided coating material may be any material which, under the conditions, adheres to the surface of the agglomerates and forms a continuous closed enveloping shell of appreciable thickness sufficient to physically support the pellet and present a substantially dry exterior. Preferably, the coating material is chemically reactive with the surface acid of the agglomerates and is either (a) a substance which is itself a plant nutrient or (b) a substance which is capable of yielding a plant nutrient upon acidulation.

As the inorganic acid material there is preferably used sulphuric or phosphoric acid or a

mixture of the two.

The pellets formed by the process of the invention though physically complete, are internally chemically reactive and subsequent to their formation are allowed to cure for from a few hours to a few days until the reactions are complete for all practical purposes and the pellets hard enough for shipment and use.

For best results from this invention the entire process, including curing, is best carried out by the method claimed in co-pending Application No. 34069/55 (Serial No. 828,881) from which this present application has been divided and according to which a fertilizer containing phosphate is manufactured by a process 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 curing goes on substantially continuously, and (b) the water content of the mass undergoing curing is such that sensibly dry free-flowing cured fertilizer product which results from the process has been dried substantially entirely by crystallization alone.

In a practical method of performing the present invention in accordance with the teachings of said copending application, hereinafter referred to as the parent application, the pellets during curing are heaped in piles, which piles are provided with ventilating passages extending thereinto such that the exothermic heat developed by the piled up pellets during curing is transmitted substantially directly to the atmosphere, the temperature of the piled-up pellets decreasing substantially continuously until the practical completion of curing. The pellets are preferably placed in such "ventilated" piles promptly after their physical completion and preferably in relatively shallow superimposed layers.

While this invention depends for its full effectiveness upon the conservation of sufficient moisture in the pellets so that it can be used for optimum crystallization which accomplishes the chemical results of the finished product with the consequent increased crop growth activity as set forth fully in the parent application and briefly summarized hereinafter, the pellets soon after their physical completion may be piled for curing in the conventional large piles without damage to their physical condition and with no reversion according to conventional standards but with some loss of

crop growth activity. However, the improved physical condition of the product of this invention and the decreased curing time outweigh this loss of activity.

The products of the present invention are uniformly-sized pellets with a negligible percentage of off-sized pellets which must be recycled, and are dry and free-flowing; as a result they may be handled, shipped and applied to the ground with improved facility. The pelleted product may be made in any desired size from a powder to granules to individual pellets of half-inch diameter or more. Herein, the term pellet is used to include all sizes of the product. The actual size of the pellets is controlled by the time of agglomeration and the amount of moisture in the mass, and, in practice, about 95% of the product is of the selected size compared with 50% or less usually achieved by prior art processes.

The phosphate content of the superphosphate product may be ~~any~~ any concentration throughout the range known as normal (say 16 to 20% P_2O_5) or enriched (say 20 to 42% P_2O_5) or triple (say 42 to 50% P_2O_5).

The phosphate rock used in this invention is any raw phosphate or phosphatic ore and an important feature of this invention is that low grade phosphate ores may be efficiently used which are too low in phosphate to be handled economically by any known processes, if at all. Furthermore, this invention can be practised effectively with phosphate ores which are high in metal impurities, particularly iron and aluminium. Previously it has been held that rocks having more than 3 to 5% of metals capable of forming sesquioxides if usable 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 and other containers in which the fertilizer is placed. However, such rocks can be acidulated according to the present invention 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, this invention makes available for easy and economical use to supply an improved product such phosphate rocks containing 5% or more of these metals.

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.

While, in the preferred process of the invention, it is usual to use high grade highly concentrated sulphuric acid and/or phosphoric acid, it is an important feature of the present invention that low grade sulphuric acids which contain impurities such as gums and oils may



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be used. Thus in the present invention a low grade acid can be employed without extensive pretreatment to remove the impurities therein. In particular, "sludge acid" which is an inexpensive sulphuric acid which has been used in the purification of petroleum products and contains oils and gums and other impurities, may be used. Previously the use of such an acid in fertilizer manufacture has resulted in a sticky product which is difficult to handle and dry. In the present invention the gummy nature of the acid is helpful to agglomeration; however, in many cases the acid potential of the sludge acid is no more than 35 to 40° B and therefore it is usually necessary to add concentrated acid to bring up the concentration to the desired level, usually between 52 and 56° B.

As an alternative to using liquid inorganic acid, the process of the invention may be performed in accordance with the process claimed in a second copending Application No. 27936/59 (Serial No. 828,883), also a divisional from said parent application and which provides, a process for the manufacture of a fertilizer product in which a solid fertilizer raw material is reacted with inorganic acid material, characterised in that said solid fertilizer raw material is reacted with a preponderantly dry acidic sludge which contains the inorganic acid material together with a fertilizer ingredient, said fertilizer ingredient and fertilizer raw material and acid material being such as to result in a dry mixed fertilizer the process being carried out in the absence of extraneously applied heat and without artificial drying of the product. A particularly useful acidic sludge used in accordance with this process is an ammoniated sludge formed by the absorption of ammonia in sulphuric acid. Other useful sludges and further details for carrying out such a process are to be found in the specification of said second copending application to which reference should be made.

So that the process of the invention may be carried out in its preferred form, it is important to choose the concentration of the acidic material, whether liquid or a preponderantly dry sludge as above, with care so that the moisture of the acid furnishes all which is utilised in the entire process, with the exception that, if a liquid fertilizer ingredient additional to phosphorus is added, allowance is made for the moisture thereby added. The concentration is preferably chosen to limit and control the amount of moisture in the agglomerates to that which by crystallization alone results in a dry coated pellet without addition or removal of any substantial amount of water throughout the entire process. Nevertheless tolerances are not close.

Although the agglomerates when formed are high in free acid they are not "over-acidulated" and, in fact, this invention is notable for its use of less than conventional amounts

of acid to convert a given amount of tricalcium phosphate to available form.

In order to give a general understanding of the basis of this increased crop growth and the novel anion in these pellets when cured as immediately above stated, the following resume of the said parent application is given.

The products hereof when cured in this preferred manner 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.

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.

Only a small portion of the phosphorus in commercial fertilizers applied to the soil is actually used by plants, although large portions of the nitrogen and potash are used. Ex-



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periments have shown that plants ordinarily use only between 10 and 20% of all phosphorus applied in commercial fertilizers.

5 Field tests show that, per unit of phosphorus applied, the product hereof when cured in the preferred manner increases plant growth from 10 to 300% over previous fertilizers. Such figures are increases over the present utilization of from 10 to 20% of the total available or water-extractable phosphorus applied. Since this invention was made in the United States of America where the official standards are based on citrate-soluble or available phosphorus, the examples hereof are of products to meet this commercial standard. Note, however, that this invention produces an unusually high percentage of water-extractable phosphorus and maintains it over long periods of time. Moreover, according to this invention the novel component hereof causes the entire phosphatic component to partake of the characteristics of its novel truly water-soluble acidic salt.

20 Another characteristic of the cured product hereof is a proportion of water-soluble calcium and water-soluble sulphate radicals which is higher than that ordinarily available from the calcium phosphate and calcium sulphate contained in known cured products, as is highly desirable for many soils.

30 The cured products hereof are further characterized by the presence of a large proportion of a novel truly water-soluble acid phosphatic radical not found in conventional fertilizers. It ionizes in solution and, in the presence of soluble metallic compounds, either in the fertilizer complex or in the soil, reacts to produce acidic phosphatic compounds of these metals. The cured products hereof contain and maintain a truly acidic soluble phosphorus salt which, upon solution within the soil, reacts to produce other salts which resist fixation.

40 Though the free acid content of the cured products hereof is not substantially greater than that of conventional products, they have a relatively greater quantity of hydrogen ions instantly available at all times and in all dilutions. This creates conditions favorable to the formation of soluble phosphatic salts without the use or presence of excess acid.

50 In order to identify the cured product hereof, crystallographic studies were made of dried water extracts (1) of the cured product, (2) of cured conventional superphosphates, and 55 (3) of synthetic mixtures of known composition. Each such water extract was treated with a standard reagent in accordance with usual crystallographic technique. One synthetic mixture was prepared which had properties almost identical with the cured product hereof, and another synthetic mixture with properties almost identical with cured conventional superphosphate. As a result of these studies, it was concluded that:

(1) The cured products hereof comprise a

mixture of monocalcium phosphate in association with a substance which responds to tests for calcium hypophosphite;

(2) The cured conventional superphosphates comprise a mixture of calcium pyrophosphate, dicalcium phosphate and monocalcium phosphate. Thus the cured product hereof is chemically distinct from cured conventional superphosphate.

This characteristic and novel substance, hereinafter referred to as "hypophosphite," itself truly water-soluble, tends to render the cured product as a whole truly water-soluble. This characteristic substance may be either calcium hypophosphite as such or a complex phosphatic substance which reacts in a manner similar to calcium hypophosphite. In any case the "hypophosphite" imparts to the cured product herein increased plant food value per unit by weight of P_2O_5 , as such units are established by conventional chemical analyses, and improved ability to remain available as plant food upon dissolution in the soil.

Further tests have shown that when a solution of the cured product hereof or of a standard substantially identical therewith is heated above $160^\circ F.$ and allowed to cool the improved properties and the characteristic chemical component of the cured product herein are destroyed. The resultant product after such heating exhibits the properties and reactions of conventional commercial superphosphate. If a solution of conventional superphosphate or of a standard substantially identical therewith is heated above $160^\circ F.$ and allowed to cool no change can be observed.

These laboratory results are confirmed by the fact that many tests have shown that plants show much greater growth when treated by the products hereof than when treated by conventional superphosphates, each of the same weight of available P_2O_5 and of the same weight of water-extractable P_2O_5 .

Crystallography was used to compare the superphosphatic product of the present invention with superphosphates of the prior art. Ordinarily inorganic chemical analysis is based upon reducing the constituents of an unknown compound to their elementary condition or converting them into some standard substance which can then be measured. Such analysis, however, does not meet a situation such as this 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. In recent years, however, this problem 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. The products hereof, however, may be subjected to conventional elemental analysis to meet all legal and commercial requirements for sale according to conventional terms.

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The above discussion applies in full only when the pellets of this invention are cured without dehydration. For further information reference is directed to the specification of said parent application.

The processes herein require less than conventional amounts of inorganic acidic material to secure a given amount of available and/or water-extractable phosphoric acid per unit of acidic material. The reason for this greater efficiency of the acidic material lies in the method herein of agglomerating and coating the product. The retention of the original moisture present when the discrete particles have been formed ready for use at the time when it is needed for optimum crystallization thus results both in a greater ratio of original conversion of insoluble phosphates of the rock to available and/or water-extractable forms per unit of acidic potential employed and also the greater permanence of such available and/or water-extractable phosphorus in the cured product.

Known processes attempt to avoid "reversion" of water-extractable P_2O_5 to citrate-soluble or unavailable (tri-basic) P_2O_5 by adding acid in great excess over stoichiometric proportions. In the processes herein this ratio is ordinarily less than stoichiometric. Nevertheless water-extractable and/or truly soluble phosphates once created in this product during a period of years do not change back to citrate-soluble or unavailable form. This permanent retention of the water-extractable component, without the use of excess acid, must not be confused with the presence herein of the characteristic and novel truly water-soluble component the radical of which is above identified and defined as calcium hypophosphite in

association with monophosphate. This saving of acid per unit of water-extractable product achieved by the processes herein are shown in the Table given in the specification of the parent application and the discussion thereof, which compare two samples of the cured product of this invention, one pelleted and one unpelleted, with two samples of the prior art.

To secure comparable results, figures for materials were reduced to pounds of sulphuric acid (60° B. at 60° F.) and of rock required to make one pound of available P_2O_5 . Since the invention originated in the United States, where available or citrate-soluble phosphoric acid is the standard, that was used, but figures for water-extractable P_2O_5 for this invention are even more favorable.

In general, the processes hereof compared with previous processes per unit of available P_2O_5 in the product:

- (1) Produce a product with higher available P_2O_5 .
- (2) Require much less acid to obtain this higher available P_2O_5 , averaging over 16%.
- (3) Require much less phosphate rock, averaging over 9%.
- (4) Are carried out with lower material costs.
- (5) Are carried out with lower operating costs.
- (6) Are carried out with lower capital expense.

In the following Table a superphosphate pellet according to the present invention is compared with three superphosphates in pelleted form made according to known practice in the art:

TABLE

	Pellet According to the Invention	Conventional Pellet		
		A	B	C
Moisture	1.25	1.66	7.7	2.78
Phosphoric Acid radical (P_2O_5)				
Total	21.8	21.12	20.50	21.47
Insoluble	.90	.88	1.18	1.10
Available	20.28	20.24	19.32	20.37
Water-extractable	18.78	15.13	13.34	15.17
Ratio water-extractable to available P_2O_5	92.1	76.35	69.04	74.52
Ratio available P_2O_5 to total	95.7	95.8	94.2	95.1
Free acid	.80	.40	1.12	1.44

The pellet of the first column is in accordance with that of Example 1, which follows, wherein the acid: rock ratio is 850:1250, as is commonly used in the practice of this invention. "Conventional pellets B and C" are made from an acid: rock ratio of 911:1150. That of A is similar. All materials are reduced to the same basis.

The above analyses illustrate the fact that the high ratio of water-extractable phosphate in this product is not due to excess acid since the total citrate-insoluble in the four products is about the same.

A portion at least of the saving in acid in this invention is associated with avoidance of waste in connection with metals which occur as impurities in phosphate ores. Also greater crop growth per unit of phosphorus is in part due to different reactions between this fertilizer and metals in the soil. Thus this presence of water when needed, and the absence of high heat, which result in the characteristic radical hereof, are associated with the avoidance of the waste of the acidic material in temporarily converting certain components of the rock, as for example iron and aluminium phosphates, to available forms which in known processes quickly revert to forms unavailable as plant food. When rocks high in metals capable of forming sesquioxides such as iron and aluminium are acidulated in accordance with the invention substantially the same proportion of acid is used as required for rocks low in these elements. The resultant product contains such metals in usable chemical combination with phosphorus. These combinations long remain readily available as plant food and the products containing them are dry and free-flowing without need for artificial drying.

Agronomists are agreed that in many soils metals, or "trace elements," in the forms that can be used by plants, are desirable and often essential. This invention supplies them in assimilable form. If desired suitable metal salts may be added to the material being processed at any stage before the coating of the pellets, if not already present in the phosphate rock, in order to make up deficiencies in particular soils. Additional fertilizer ingredients which may be added include, for example, salts of aluminium, iron, copper, magnesium, manganese, zinc, barium, chromium, cobalt, nickel and strontium. Particular mention may be made of magnesium, which may be added to the reaction mixture as dolomitic limestone and thereby readily made available for plant utilization.

Other additional fertilizer ingredients additional to phosphorus, particularly those contributing nitrogen or potassium, may be added during the process of the invention either in finely-divided dry form or in moist or liquid form. The additives may be premixed with the acidic discrete particles or, preferably, they may be added to the particles at the start of

the agglomerating operation and mixed intimately by the movement thereof. This mixing must be completed before the commencement of the coating operation. The coating material is applied to the moist acidic surfaces of the compound agglomerations completely to cover them and to physically complete the pellets. Among the dry finely-divided additives which can be used, the following may be named for example only: ammonium sulphate, ammonium nitrate, urea, potassium nitrate, potassium chloride, or potassium sulphate.

An important source of nitrogen is an ammoniated liquid which may be added to the discrete particles prior to the agglomerating operation. It must not be of such quantity as will cause the discrete particles to coalesce and must be neutralized as by sulphuric or other acid before contact with the acidic particles, otherwise high heat and dehydration will result, thus resulting in an inferior product.

In all cases, sufficient moisture must be present in the discrete particles and the additives to supply that which is necessary for successful agglomeration and insufficient moisture to furnish a surplus over that which will be taken up as water crystallization. The moisture content of the agglomerations is determined solely by that which is present in the discrete particles and in the additives which are mixed therewith. To compensate for moisture added by the other ingredients, it is merely necessary to decrease the moisture supplied by the inorganic acidic material used in the primary reaction by increasing its concentration and, conversely, if more moisture is required to agglomerate dry ingredients, it is merely necessary to increase the moisture in the acidic material by decreasing its concentration. The necessary adjustments are clear to any experienced fertilizer technician.

In a practical and preferred method of performing the process of the present invention, 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



and from which the mixture was dumped } h →



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 other 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 and the reaction product is then formed into discrete particles, generally fine.

In general, any effective method, whether continuous or otherwise, may be employed to mix the ground phosphate rock and the selected acid, to permit the mixture to set, and to disintegrate the set mixture provided the resultant particles are moist and acidic and are still tending to set and develop heat.

When the primary chemical reaction is substantially complete, i.e. when the reaction mass has hardened sufficiently to be disintegrable without coalescing, the mass is formed into discrete particles. These discrete particles, which are still tending to set and develop heat, are then moved upon themselves, with or without an additional fertilizer ingredient being added, the free moisture remaining from the primary reaction being sufficient to form the particles and additional fertilizer ingredient, if any, into small agglomerates approaching the size of the pellets desired and having acid-wetted exterior surfaces. This agglomerating operation may be carried out in any convenient mechanical device which causes the moist particles to adhere to each other, usually a conventional pelleting drum. When the agglomerates have been built up to the desired size a dry finely-divided absorptive material and preferably one which is reactive with the surface acid of the agglomerates, is added and movement continued until the moist exterior surfaces of the agglomerates are well coated. During agglomeration and coating dehydration and external heating of the material being processed are unnecessary and harmful.

The coating material is applied only to the external surfaces of the agglomerates and even though it is preferred that the coating material is chemically reactive with and becomes chemically bonded to the surfaces of the agglomerates and dries them, the coating does not penetrate the mass. This operation therefore must not be confused with the known practice of incorporating dry material within the body of a mass which is to be formed into a pellet. Such incorporation defeats the purpose of this invention. The coating and its co-action with the surface moisture of the agglomerates alone transform them into physically completed pellets which almost immediately become sensibly dry and saleable

while permitting chemical activity to continue within the interior of the pellets. The product is physically complete as it comes from the coating operation. Subsequent chemical action in the interior of the pellets encased in their characteristic coatings further rapidly increases the plant food as curing continues.

Any finely-divided absorptive material can be used as coating, but one which itself is a plant nutrient or is capable of yielding a plant nutrient upon acidulation and reacts chemically with the pellet is preferred. Among the suitable coating materials are: ground phosphate rock, mixtures of phosphate rock and charcoal, ground dolomite, bone black, bone char, lamp black, nitrogen-bearing organic materials including animal tankage and cottonseed meal, and potassic and phosphatic dusts. The amount of coating material employed differs slightly according to its character, the concentration of the acid, and the desired results but 5% (by weight) of the total finished material is usual, although as little as 3% and as much as 10% or more may be used.

The novel pellet of the processes herein is preferred to as "closed" because its surface does not present sensible pores.

The pellets will be further described with reference to the accompanying drawings in which:

Fig. 1 is a reproduction of a photomicrograph enlarged about 30 diameters of the exterior of a single simple pellet of superphosphate made in accordance herewith and of the type called a "closed pellet";

Fig. 2 is a reproduction of a photomicrograph enlarged about 30 diameters of the exterior of an aggregate pellet which is made up of a plurality of smaller simple pellets which have adhered to each other.

Fig. 3 is a reproduction of a photomicrograph enlarged approximately 6 diameters of a group of closed pellets of the type shown in Fig. 1; and

Fig. 4 corresponds to Fig. 3 but shows a group of closed pellets of an aggregate form.

In its simple form as shown in Figs. 1 and 3, the shape of the pellet is an approximation of spherical to ovoid, but this general form is subject to wide variation. Often the shape is somewhat angular. Pellets hereof are differentiated from pellets produced by fragmentation of a larger mass by having a continuous closed enveloping shell. Microscopic examination shows that these pellets consist essentially of this outer shell which has appreciable thickness and compact structure and which is free from sensible pores and an interior of reticulated crystalline material in massive glassy form. The interior has numerous continuous inter-connecting spaces such as would normally be formed following crystallization of a saturated solution confined in a limited volume. In the course of manufacture, while the material is being moved upon itself, several

simple agglomerations often stick together to make up aggregates or compound agglomerations which are then covered by a single coating. Such pellets are illustrated in Figures 2 and 4.

Almost all of the products of this invention as they come from the pelleting drum are of uniform size. In practice these pellets often are so uniform that they are delivered to the farmer without sizing. If sized the amount larger than a screen opening of the A.S.C. number 5 (0.157 inch) or smaller than number 30 (0.0234 inch) on said scale ranges from a rare maximum of 5% down to a common figure of less than $\frac{1}{2}$ of 1%, with the great majority of the pellets "through 8 on 20" that is less than 0.094 inch and greater than 0.0331 inch. The small amount of over-sized material, which is still fairly soft, may be crushed as between rubber rollers and with the under-sized particles re-introduced at the entrance end of the drum. This material, if any, thus re-cycled is relatively small and plays no part whatever in the processing. Where non-pelleted fertilizers are saleable, it may be cured, put through a "breaker," and sold as fine superphosphate.

The size of the pellets can be controlled as desired within a wide range as from small granules to pellets of such size that when sown from airplanes as for rice fields or rough grazing land they will not be unduly scattered by the wind. The size depends upon the moisture in the acidic material and/or the duration of the agglomerating operation. The greater the moisture and/or the longer the duration of the agglomeration the larger the pellet and vice versa.

After the pellets have been physically completed by the agglomerating and coating just described they may be stored for curing in any known manner but preferably in accordance with the teachings of the parent application. They harden rapidly and shortly after the pelleting operation is complete can bear considerable weight. Danger of crushing in a pile of reasonable depth shortly disappears. When cured they meet all known strength tests. Even when the pellets hereof are not cured in the preferred manner they partake in some measure of the crop-producing advantages described in the parent application. The pellets hereof, after agglomeration, are less hot than fine superphosphate, the cure has proceeded further in spite of the brevity of the agglomerating process, the enclosing casing of each pellet permits crystallization to proceed rapidly and with little escape of moisture, and in the pile the passage of greater amounts of air between the pellets than with solid fine material tends to prevent overheating with consequent moisture loss. These factors, even in high piles, tend to permit the mass of pellets to cool more rapidly and with less dehydration than fine superphosphate.

However, in order to secure the full chemical advantages of the process of the parent application, the pellets after their physical completion should be piled in a "ventilated-pile" as described in the parent application so that the heat of the secondary reactions is transmitted substantially directly to the atmosphere and there is no dehydration. As described therein, the ventilated-pile may be formed by piling the pellets in formation in successive shallow layers each, for example, about 1 foot deep. Generally when pellets for a second layer come from the agglomerating and coating operation the pellets of the first layer will have cooled and hardened sufficiently so that there will be no heat absorption and dehydration or crushing. Thus a succession of layers of any reasonable number may be built up. Such layered piles may be left as long as convenient. Alternatively, the pellets may be placed in formations consisting of small piles of dimensions such that no portion of the interior is more than about 3 feet from the atmosphere and left for five or six hours. Thereafter they may be piled indiscriminately.

As will be understood by technicians experienced in the handling of any superphosphatic fertilizers, exothermic heat of the secondary reactions differs according to the formulations and materials used, but the novel principles and limits stated herein will enable any skilled worker to accomplish the full results of the preferred process.

The pellets will be sufficiently cured within two or three days so that they may be shipped and sold. In some instances, immediately after pelleting they have been shipped in relatively shallow layers, say not over 3 feet, and actually used by farmers within about a day and a half after agglomeration with excellent results. Ordinarily three days to a week of cure is recommended if sulphuric acid is used and slightly longer with phosphoric.

Though the process of the invention has previously been described mainly with reference to the production of pellets of normal superphosphate from phosphate rock and sulphuric acid, the processes of the invention with no change in principle may be applied to the production of pellets of triple or enriched superphosphate. "Enriched superphosphate" may contain over 20% and less than 50% P_2O_5 if made from rock of normal phosphorus content or have no more than 16 to 20% P_2O_5 if it is made from phosphate rock so low in phosphate that by other processes a physically and economically satisfactory product is impossible. Even if very small "pellets" of triple superphosphate are wanted, this process retains its advantages, as of economy and simplicity.

All of these procedures are carried out interchangeably with the making of normal superphosphate, with the same equipment in the same plant, with the substitution of phosphoric for all or a part of the sulphuric acid. Since,



according to this invention, the manipulative steps are the same, although as usual in fertilizer manufacture, the cost of phosphoric acid is greater than sulphuric, the total net cost per unit of P_2O_5 in the finished products of this type, according to this invention, is no more and often is less than the cost per such unit in normal conventional superphosphate. Known processes for the production of triple or enriched superphosphate, however, require capital and production costs per unit which are much greater than those for products of normal concentration.

In certain known wet processes for making triple superphosphate concentrated phosphoric acid is mixed with all of the phosphate rock which is to be acidulated. The mixture thereupon sets into a block so hard that it can be disintegrated only with great difficulty. A common alternative is to use phosphoric acid of such low concentration that the mass must be handled as a slurry and be artificially dried and then generally subjected to a long curing process. There are many variants of this process, in some of which the slurry is formed into pellets and dried.

In the process of this invention, all of the acid necessary for the acidulation of the entire product is mixed with the phosphate rock and as soon as the reaction mixture has hardened sufficiently to be disintegrable, the mixture is broken up into discrete particles which are still tending to set and develop heat and then the discrete particles are agglomerated and the coating material is applied to them. Consequently the original digestion mass does not set hard enough to cause difficulty in disintegration. At no time in any embodiment of this invention except shortly after the original mixing is there a slurry and at no time is extraneous heat applied. Subsequent curing of the pellets takes longer than for normal superphosphate by from 1 to 5 days.

For the production of enriched and triple superphosphate mixed phosphoric and sulphuric acid is generally used. Usually the mixture is of phosphoric acid of low concentration, for example $30^\circ B$ (slightly over 40% H_3PO_4) used as a diluent for sulphuric acid of from 60° to $66^\circ B$.

The following examples illustrate the process of the invention as applied to the production of pelleted normal, enriched and triple superphosphate.

EXAMPLE 1

To prepare a normal superphosphate in pelleted form by a process herein mix;

850 lbs. sulphuric acid calculated at $60^\circ B$, at $60^\circ F$. and use at from 52° to $56^\circ B$.

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

Prepare 100 lbs. ground rock for coating.

The concentration of the acid, preferably

within the above limits, can easily be determined by those skilled in the superphosphate art in accordance with common factors in the fertilizer industry such as the characteristics of the particular rock, including phosphatic and carbonate content, and other usual variants. If the concentration of the acid is such as to secure good conventional superphosphate it will be satisfactory for this novel pelleting process. With Florida pebble rock of ordinary characteristics the concentration usually employed is 55° or $56^\circ B$, although for pellets predominantly larger than about one-tenth of an inch acid of from 52° to $54^\circ B$ may be used.

The ratio of acid ($60^\circ B$.) to rock (including coating) used to prepare the product thereof is 850:1250. 2.15 lbs. of $60^\circ H_2SO_4$ according to this Example produces 1 lb. of available P_2O_5 while according to representative known pelleting processes which apply heat and dehydration 2.605 and 2.624 lbs. of $60^\circ H_2SO_4$ are required for each pound of available P_2O_5 . The ratio of water-extractable to total available phosphoric acid according to this process is and remains 92—94% or above. If a higher water-extractable ratio is desired the amount of acid is increased. According to known processes the ratio of acid to rock (correspondingly adjusted for acid concentration) is much higher, with a much lower maintained ratio of water-extractable to total available phosphoric acid. Cf. the Table previously given.

Mix rock and acid in the usual uninterrupted way and after setting form discrete particles and then follow the above described agglomerating and coating procedure. Move the particles upon themselves until agglomerations of a desired size with acid-wetted surfaces are formed and then in the final stage of the agitation while continuing it add the additional 100 lbs. of ground rock. This ground rock adheres to these surfaces only and acts as a coating thereby finishing the pellets. For illustration, it is stated that the agglomerating operation in an inclined rotating pelleting drum may take no longer than about four minutes, with from fifteen to forty seconds to add the coating. The time will depend upon the concentration of the acid, the rate of rotation and inclination and the size of pellets desired. Average output per drum may be taken for purposes of illustration only as about forty tons per hour.

A convenient method of obtaining another fertilizer ingredient, in this case organic nitrogen applied as a coating, together with the other valuable ingredients, is illustrated as follows:

EXAMPLE 2

Prepare a 7-12-7 mixed pelleted homogeneous fertilizer according to the following formulation

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- 200 lbs. animal tankage 10 N changed to achieve the necessary physical consistency, this exact ratio being a matter more of physical than chemical consideration. 65
- 1270 lbs. freshly mixed super-phosphate 18.5 P A typical analysis:
- 210 lbs. potassium nitrate 14 N 39 K
- 215 lbs urea 47 N
- 20 lbs. diammonium phosphate 21 N 24 P
- 85 lbs. potassium chloride 52 K
- | | Per cent |
|----------------------------|----------|
| Moisture at 100°C. | 5.35 |
| Total P_2O_5 | 50.20 |
| Insoluble P_2O_5 | .04 |
| Available P_2O_5 | 50.16 |
| Water-extractable P_2O_5 | 49.25 |
- 10 Prepare discrete particles of freshly mixed superphosphate, which particles are still moist and acidic, and tending to set and develop heat, and add all of the other ingredients, except the animal tankage, either shortly before agglomerating or early in the agglomeration operation. Apply the animal tankage as coating after the agglomerations have reached the desired size.
- 15 The product of this example at low cost supplies nitrogen largely in organic form. Also in known processes urea was considered useable in proportions no greater than 50 pounds per ton of mixed fertilizers. A pelleted product according to this invention may include urea in quantities up to 500 pounds per ton of product. Other hygroscopic ingredients may be used in larger than known proportions in this invention.

EXAMPLE 3

- 30 To make one (short) ton of triple superphosphate, divide 813 pounds of ground phosphate rock into two parts, one of 713 pounds for the body of the pellets and the other of 100 pounds for the coating. Mix the larger quantity in an ordinary superphosphate mixing pan or the like in the ordinary way with 1227 pounds of phosphoric acid of 87%, used as at from 70 to 75%.

From the completion of this mixing, this mass may be handled in one of two ways:

- 40 1. The mass may be placed in a den where it is left for a few minutes until it hardens sufficiently. It then can be mechanically disintegrated as easily as ordinary superphosphate and passed while still hot and steaming into a pelleting drum or its equivalent. Thereupon the disintegrated acidic particles are moved upon themselves to form agglomerations with acid-wetted surfaces. Then, when the desired size has been reached, the additional hundred pounds of phosphate rock is added. Under continued agitation this added rock adheres to the surface and physically absorbs the surface acid to physically complete the pellets.
- 45 2. A screw conveyor slowly moves this digestion mixture directly from the mixing pan to a disintegrator and pelleting device omitting the intermediate step of hardening in a stationary den, an operation which need take only a few minutes.
- 50 This intermediate product (after the mixing and before pelleting) is sufficiently plastic to be readily handled mechanically. The ratio of the one portion of rock to the other can be

- EXAMPLE 4
- 75 To produce one (short) ton of enriched superphosphate of 30% P_2O_5 , 955 pounds of ground phosphate rock, 75% bone phosphate of lime, are digested by a mixed acid of 440 pounds of 66°B. H_2SO_4 diluted with 676 pounds of 30°B. H_3PO_4 , allowed to set and disintegrated. Thereafter as before described, the disintegrated particles while hot and steaming are moved upon themselves and the acid-wetted agglomerates thus formed are coated with 100 pounds of additional dry fine phosphate rock.

In conclusion, the advantages of the process of this invention over previous processes may be summed up in that the process may be carried out: (1) more simply; (2) more rapidly; (3) with fewer personnel; (4) with greater conversion of insoluble phosphate to permanently soluble forms per unit of acidic material; (5) from less expensive materials often otherwise unusable; (6) with less and inexpensive equipment with adaptability to existing conventional plants at minimum expense; (7) with no externally applied heat; (8) with less power; and (9) with less careful control.

WHAT I CLAIM IS:—

- 100 1. A process for the manufacture of a pelleted fertilizer containing phosphate which comprises providing small discrete particles of the product of the primary reaction between an inorganic acid material and phosphate rock, the surfaces of which particles are moist and acidic, moving the discrete particles 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, coating the agglomerates with 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. 125
2. A process according to Claim 1, wherein



200 lbs. animal tankage	10 N
1270 lbs. freshly mixed superphosphate	18.5 P
210 lbs. potassium nitrate	14 N 39 K
215 lbs urea	47 N
20 lbs. diammonium phosphate	21 N 24 P
85 lbs. potassium chloride	52 K

changed to achieve the necessary physical consistency, this exact ratio being a matter more of physical than chemical consideration.

A typical analysis:

	Per cent
Moisture at 100°C.	5.35
Total P_2O_5	50.20
Insoluble P_2O_5	.04
Available P_2O_5	50.16
Water-extractable P_2O_5	49.25

Prepare discrete particles of freshly mixed superphosphate, which particles are still moist and acidic, and tending to set and develop heat, and add all of the other ingredients, except the animal tankage, either shortly before agglomerating or early in the agglomeration operation. Apply the animal tankage as coating after the agglomerations have reached the desired size.

The product of this example at low cost supplies nitrogen largely in organic form. Also in known processes urea was considered useable in proportions no greater than 50 pounds per ton of mixed fertilizers. A pelleted product according to this invention may include urea in quantities up to 500 pounds per ton of product. Other hygroscopic ingredients may be used in larger than known proportions in this invention.

EXAMPLE 3

To make one (short) ton of triple superphosphate, divide 813 pounds of ground phosphate rock into two parts, one of 713 pounds for the body of the pellets and the other of 100 pounds for the coating. Mix the larger quantity in an ordinary superphosphate mixing pan or the like in the ordinary way with 1227 pounds of phosphoric acid of 87%, used as at from 70 to 75%.

From the completion of this mixing, this mass may be handled in one of two ways:

1. The mass may be placed in a den where it is left for a few minutes until it hardens sufficiently. It then can be mechanically disintegrated as easily as ordinary superphosphate and passed while still hot and steaming into a pelleting drum or its equivalent. Thereupon the disintegrated acidic particles are moved upon themselves to form agglomerations with acid-wetted surfaces. Then, when the desired size has been reached, the additional hundred pounds of phosphate rock is added. Under continued agitation this added rock adheres to the surface and physically absorbs the surface acid to physically complete the pellets.

2. A screw conveyor slowly moves this digestion mixture directly from the mixing pan to a disintegrator and pelleting device omitting the intermediate step of hardening in a stationary den, an operation which need take only a few minutes.

This intermediate product (after the mixing and before pelleting) is sufficiently plastic to be readily handled mechanically. The ratio of the one portion of rock to the other can be

EXAMPLE 4
To produce one (short) ton of enriched superphosphate of 30% P_2O_5 , 955 pounds of ground phosphate rock, 75% bone phosphate of lime, are digested by a mixed acid of 440 pounds of 66°B. H_2SO_4 diluted with 676 pounds of 30°B. H_3PO_4 , allowed to set and disintegrated. Thereafter as before described, the disintegrated particles while hot and steaming are moved upon themselves and the acid-wetted agglomerates thus formed are coated with 100 pounds of additional dry fine phosphate rock.

In conclusion, the advantages of the process of this invention over previous processes may be summed up in that the process may be carried out: (1) more simply; (2) more rapidly; (3) with fewer personnel; (4) with greater conversion of insoluble phosphate to permanently soluble forms per unit of acidic material; (5) from less expensive materials often otherwise unusable; (6) with less and inexpensive equipment with adaptability to existing conventional plants at minimum expense; (7) with no externally applied heat; (8) with less power; and (9) with less careful control.

WHAT I CLAIM IS:—

1. A process for the manufacture of a pelleted fertilizer containing phosphate which comprises providing small discrete particles of the product of the primary reaction between an inorganic acid material and phosphate rock, the surfaces of which particles are moist and acidic, moving the discrete particles 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, coating the agglomerates with 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.

2. A process according to Claim 1, wherein

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- the initial concentration of the acid material is such that there results firm physically completed sensibly dry free-flowing pellets, the interiors of which have dried substantially entirely by crystallization alone, substantially no water being added or removed from the material being processed throughout the entire process.
3. A process according to Claim 1, wherein a fertilizer ingredient additional to phosphorus is added to the material being processed before or during agglomeration and before coating.
4. A process according to Claim 3, wherein the additional fertilizer ingredient is added in finely-divided dry form, allowance being made for the relative decrease in moisture content of the material being processed.
5. A process according to Claim 4, wherein the additional fertilizer ingredient is ammonium sulphate, ammonium nitrate, urea, potassium nitrate, potassium chloride or potassium sulphate.
6. A process according to Claim 3, wherein the additional fertilizer ingredient is added in moist or liquid form, allowance being made for the increase in moisture content of the material being processed.
7. A process according to Claim 6, wherein the additional fertilizer ingredient is an ammonium product substantially neutralized by the addition thereto of a mineral acid.
8. A process according to any one of the preceding claims, wherein the finely-divided coating material is reactive with the surface acid of said moist and acidic particles.
9. A process according to any one of Claims 1—7, wherein the finely divided coating material contains (a) a substance which is itself a plant nutrient or (b) a substance which is capable of yielding a plant nutrient upon acidulation.
10. A process according to any one of Claims 1—7, wherein the finely divided coating material is ground phosphate rock, ground dolomite, charcoal, bone black, bone char, lamp black, a nitrogen bearing organic material including animal tankage and cottonseed meal, or a potassic or phosphate dust.
11. A process according to any one of the preceding claims, wherein the inorganic acid material is sulphuric acid.
12. A process according to Claim 11, wherein the sulphuric acid is a low grade sulphuric acid.
13. A process according to any one of Claims 1—10, wherein the inorganic acid material is phosphoric acid.
14. A process according to any one of the preceding claims, wherein the phosphate rock contains metallic substances capable of forming sesquioxides or 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.
15. A process according to any one of the preceding claims, wherein the small discrete particles of the product of the primary reaction between the inorganic acid material and the phosphate rock are provided by mixing said acid material and rock, the resultant 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 mass, subsequent further hardening as well as curing of the mass so broken up taking place.
16. A process according to Claim 15, wherein, additionally, after the physical completion of the pellets, curing takes place at normal pressure and wherein, from the time the mass is 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 there results a cured sensibly dry free-flowing pelleted fertilizer product which has been dried substantially entirely by crystallization alone.
17. 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.
18. A process according to Claim 17, wherein the acidic sludge is an ammonium product formed by the absorption of ammonia in sulphuric acid.
19. A process according to Claim 16, wherein the pellets during curing are heaped in piles, which piles are provided with ventilating passages extending thereinto such that the exothermic heat developed by the piled-up pellets during curing is transmitted substantially directly to the atmosphere, the temperature of the piled-up pellets decreasing substantially continuously until the practical completion of curing.
20. A process according to Claim 19, wherein said pellets after physical completion are successively piled-up in relatively shallow superimposed layers.
21. A superphosphatic pellet when prepared by a process as claimed in Claim 1, having an enveloping shell united with its internal mass, said shell being of compact structure and appreciable thickness and free from sensible pores.
22. A superphosphatic pellet according to Claim 21, wherein said shell surrounds and is supported by an interior mass of reticulated crystalline material in massive glassy form.
23. A superphosphatic pellet according to Claim 22, wherein said reticulations are penetrated by continuous spaces, a major portion of said spaces being interconnected and of the character formed following the crystallization from a heavy saturated solution confined with-



phosphatic/



in limited space.

5 24. A pelleted superphosphatic fertilizer according to Claim 21, in which each pellet is an aggregate of a plurality of discrete smaller pellets adhering to each other by the crystallization of their adjacent outer surfaces which thereby form a continuous shell enveloping the entire aggregate.

10 25. A pelleted superphosphatic fertilizer when prepared by a process as claimed in Claim 1, which in solution yields an acid salt

which responds to tests for hypophosphite in association with monophosphate.

26. The process of manufacturing a pelleted superphosphatic fertilizer substantially as hereinbefore described. 15

27. A pelleted superphosphatic fertilizer substantially as hereinbefore described with reference to the accompanying drawings.

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