

PATENT SPECIFICATION

NO DRAWINGS

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828.883

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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, W.C.1] 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:—

10 2/ This invention relates to processes for the preparation of mixed fertilizers, i.e. fertilizers which provide, in available form, two or more plant-nutritive elements, at least one of which is a primary plant-nutritive element, viz. phosphorus, potassium or nitrogen.

15 2/ In accordance with the invention 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 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, 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.

20 35 The term "fertilizer raw material" used in this specification means a material which contains a plant-nutritive element, not necessarily a primary plant-nutritive element, and which, as a result of the reaction with inorganic acid material, is rendered useful or more useful as a plant nutrient. Specific fertilizer raw materials are phosphate rock and dolomitic limestone, alone or in combination.

The term "fertilizer ingredient" as used in this specification, means any ingredient which is useful *per se* as a fertilizer as opposed to an ingredient requiring chemical conversion before becoming useful.

As acidic sludges there may be used any sludge or combination of sludges containing an inorganic acid material, such as sulphuric acid and/or phosphoric acid, and a fertilizer ingredient.

The fertilizer ingredient may contain one or more of the following plant-nutritive elements, viz. nitrogen, phosphorus, potassium, calcium, magnesium or sulphur. In the simplest case the sludges may be prepared by mixing the fertilizer ingredient with the acid material, but preferably the sludge is formed by reacting a suitable precursor of the fertilizer ingredient with excess acid, for example, by reacting ammonia or potassium chloride with excess sulphuric acid to form, respectively, an ammonium sulphate/sulphuric acid sludge and a potassium sulphate/sulphuric acid sludge. If necessary, additional acid may be added to the sludges so formed to bring the acid potential up to the level required to acidulate the whole of the fertilizer raw material.

It is an essential characteristic of the invention that the sludge does not contain sufficient moisture as to be a slurry which can be pumped, but is a preponderantly solid mass which is palpably moist. During an early stage of its formation it may pass through a liquid stage but it soon partakes chiefly of the characteristics of dry material, as does a mixture of phosphate rock and liquid acid. As illustrative only it may be said that this sludge may have three parts by weight in the dry phase and one part in the wet phase. Certain of these sludges resemble fine wet sand in which is often termed a "drip-dry" condition.

All that is required to carry out the acidulation of the raw material is for the sludge

[Price 3s. 6d.]





and the ground raw material to be mixed in a manner generally known in fertilizer technology as "dry-mixing". After the physical mixing is completed the acid is allowed to permeate the mass for a short while, but it is generally not necessary to place the mixture in a den, whether of the stationary type or the continuous type, to set as is the case in many fertilizer processes particularly those using slurries. No extraneous heat is applied at any stage in the process nor is any artificial drying of the product required, and, furthermore, it is not necessary either to employ any neutralization step or any extensive curing period, one short cure, if any, is all that is needed.

The process of the invention may thus be carried out in relatively simple and inexpensive apparatus and without the highly skilled technical management which is required in the great majority of conventional processes for making mixed fertilizers. Furthermore, the process is carried out in a greatly reduced time since there is no requirement for any drying operations, the sludge providing substantially all the moisture required at any time for securing the needed chemical reactions but not to excess, and with lower handling costs since the circulating load is substantially that of the finished product.

At any time during the mixing of the sludge or the subsequent dry-mixing of the sludge and raw material, additional fertilizer ingredients in dry form such as potassic or nitrogenous material, or metallic salts useful for plant-growth, may be added to produce a three or more component mixed fertilizer. Such metallic salts may, of course, already be present in the fertilizer raw material.

At the end of the mixing operation and after the acid has been allowed to permeate the mass, the mixed fertilizer product may be broken up, pelleted if desired, and stored or otherwise handled ready for use.

When processing phosphate rock, which may be any raw phosphate or phosphatic ore, it is preferred that the process be performed and the product cured according to the process claimed in copending Application No. 30469/55 (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 comple-

tion 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.

In a practical method of performing the present invention in accordance with the teachings of said copending application, hereinafter called the parent application, and to achieve the full agronomic benefits as set forth in the specification thereof, the reaction mixture, when it has hardened sufficiently to be disintegrable without coalescing, is broken up and heaped in piles, which piles are provided with ventilating passages extending thereinto such that the exothermic heat developed by the broken up mass during curing is transmitted substantially directly to the atmosphere the temperature of the broken-up mass decreasing substantially continuously to the practical completion of curing. For further details of such method, reference is directed to the specification of said parent application.

More preferably still, the product from the reaction of the acidic sludge and a phosphate rock is disintegrated into discrete particles and pelleted by the process claimed in a second copending application, No. 27464/59 (Serial No. 828,882), also a divisional from the parent application and according to which a pelleted fertilizer is manufactured by a process 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 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 a 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 pellets but it is preferred that the coating material is reactive with



application

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 forming such a pelleted fertilizer reference is directed to the specification of said second copending application.

Perhaps the most useful fertilizer ingredients used in the acidic sludges of the present invention are nitrogen (ammonia), phosphorus and potassium, as well as sulphur and calcium.

A nitrogen-bearing inorganic acidic sludge particularly useful for the practice of this invention is obtained as a by-product of the destructive distillation of coal. In known processes of making ammonium sulphate, after the ammonia in sulphuric acid used for purification of gas or other similar purposes has been trapped, the resulting slurry is ordinarily centrifuged and then neutralized with material having no fertilizer value. Thereafter, it is sold as finished ammonium sulphate which is the most widely used source of nitrogen throughout the world in mixed fertilizers made from finished ingredients. These known practices mix ammonium sulphate and superphosphate, each a completely finished dry product, to form a mixed fertilizer containing nitrogen and phosphate. This mixture often must also be neutralized and cured for a short period. According hereto a combined product containing both fertilizer ingredients is made in a single operation with no neutralization by any material which is of no use to plant growth.

According to the processes herein sulphuric acid in a by-product operation is utilized in a purification operation to trap ammonia until approximately 75% of the acidic ammonium sulphate is in solid form and the acidic potential of the entire mass is at least 52° B. This operation preferably is carried beyond the usual point past the point of saturation and by the employment of an acid which is of higher concentration than usually employed more ammonia is trapped and a more solid sludge formed. Contrary to conventional practice 15% or more nitrogen can be trapped because the operation carries the absorption beyond the point at which the sulphate of ammonia in the sulphuric acid acts as a diluent. Use of sulphuric acid in this unusually high degree of concentration for such a purpose is economically possible because it quickly traps the maximum amount of ammonia and by the following steps all of the acid potential is properly employed. Alternatively any ammoniacal solution may be fed through relatively concentrated sulphuric acid beyond the point of

saturation as above. Phosphoric acid may be used in place of sulphuric thereby increasing the phosphatic component of the mixed fertilizer. After the ammonia is trapped and the high heat of the primary reaction has passed the quantity of fertilizer raw material necessary to utilize the acidic potential is mixed with the mass. If the product is to be fine all of the phosphate rock may be mixed with the sludge at one time. If the product is to be pelleted, as is preferred, the phosphate rock is added in two increments, one to bring the original mixture to the point at which it will agglomerate readily, and the other to coat the agglomerations when made. Ammonium sludge so produced may be mixed with other acidic sludges, as later described herein. If a potassic sludge is added, a complete fertilizer results. Such practices produce finished mixed fertilizers at a reduced cost in labor and capital and in shorter time.

For many purposes, particularly when the manufacture of mixed fertilizers is carried out in small manufacturing establishments without extensive equipment commercial ammonium sulphate may be mixed with sulphuric and/or phosphoric acid to form an acidic sludge of the above characteristics and thereupon the fertilizer raw material may be added. Since the addition of the raw material to the preponderantly dry sludge is mechanically simple and the mass does not set hard it can be formed into agglomerations and coated with equipment designed for substantially dry products and much more simple than that of a conventional superphosphate plant. One may advantageously mix sulphuric acid with commercial ammonium sulphate and handle the resulting mixture as hereinabove described.

EXAMPLE 1

Absorb 269 pounds of ammonia in 1423 pounds of sulphuric acid calculated at 60° B. and 60° F. and preferably used at that concentration. Mix intimately with 530 pounds of phosphate rock. The acidic potential of the mixture as the rock is introduced should be at least 52° B. and the high heat of the ammonia absorption should have subsided. The absorption operation is carried beyond the point of saturation at which solid ammonium sulphate appears and is continued until the ratio is substantially 3 parts of solid ammonium sulphate or more to 1 part by weight of free liquids. After the completion of the primary chemical reaction, form the mixture into discrete particles and by movement upon themselves forms agglomerations and coat them with 120 pounds of additional rock and preferably cure the pellets in accordance with the teachings of said parent application. Alternatively, if fine superphosphate is wanted, use a total of 650 pounds of rock in the original mixture. with ordinary Florida rock of 72% bone phosphate of lime the resulting product analyses 11.25—9.43—0. A total of 650 pounds of rock



Cap. "W"

is used instead of the theoretical total of 623 pounds because of the greater acidulating potential of the sulphate.

- 5 Other fertilizer ingredients in dry form may be added to the ammonia sulphate sludge as, for example, potassium, in order to make a complete three-element product, as is illustrated as follows:—

EXAMPLE 2

- 10 Prepare 2625 pounds of sludge as in Example 1. Add 1112 pounds of ground phosphate rock and 667 pounds of dry potassium chloride. Mix. At the completion of the primary reaction disintegrate, then agglomerate and add 200 pounds of ground phosphate rock as coating when the agglomerations approach the desired size. The result is a complete mixed fertilizer of an approximate analysis of 8.2—9.5—8.7. If a fine fertilizer
- 15 is desired the sludge and the dry materials may be more slowly mixed, without subsequent agglomeration. No appreciable amount of hydrogen chloride will be released because the sulphuric acid is not in excess.

- 20 Another sludge which may be used in the process of the invention is a low-chlorine potassium sludge, formed by reaction of potassium chloride with sulphuric acid. Such a sludge serves as the basis of a potassium-phosphate mixed fertilizer which may contain as little as 2% of chlorine. Chlorine in sub-

stantial quantities or for often repeated heavy applications is considered injurious to many plants, but a product with as little chlorine as 2% is accepted without question. Potassium chloride is the form in which a large proportion of all potassium in use for fertilizer material is mined and sold. Known processes convert potassium chloride to potassium sulphate by mixing for many hours with sulphuric acid under high heat. Such costly products have been referred to and are officially designated in many countries as potassium sulphate although containing 3% or more of chlorine in the total fertilizer.

To form a low-chlorine potassium sludge for use in the process of the invention, a large excess of concentrated sulphuric acid is added to the potassium chloride, and the mixture stirred for a few minutes and in the absence of externally applied heat to evolve chlorine as hydrogen chloride and to produce an acidic potassium sludge. After the chlorine is evolved and removed, this acidic sludge is used to acidulate ground phosphate rock. The excess of concentrated sulphuric acid acting on the potassium chloride drives off any desired amount of the chlorine up to about 94%. It is preferred to use 52 to 60° B. sulphuric acid. The following table illustrates the removal of chlorine:—

	H ₂ SO ₄ 60° B.	KCl	Cl Removed	%	Acid Consumed	Acid Unused	Rock Used	P ₂ O ₅ %	K ₂ O %
	100	10	4.4	93	7.92	92.1	138	18.9	2.5
65	100	30	11.35	80	20.43	79.57	119	16.7	7.7
	100	60	21.28	75	38.34	61.66	92.5	13.7	16.1

All values except as noted are in pounds.

- After having chosen the proportions of sulphuric acid and potassium chloride according to the relations indicated above, the acid and potassium chloride are mixed and stirred for a few minutes. If a fertilizer raw material other than phosphate rock, which has an "acid-rock" factor of 2.3, is used, other values must be changed accordingly. The evolved hydrogen chloride gas is passed through a water bath to form hydrochloric acid, which is sold as a by-product.

- 70 The sludge produced contains KHSO₄ and H₂SO₄ with some K₂SO₄ and a slight amount of HCl which has not been completely removed as well as the KCl from which the chlorine has not been evolved. An amount of fertilizer raw material sufficient to utilize the total acidic potential is then mixed with the acid potassium sludge. After the primary chemical reaction is complete, the mass preferably is made into agglomerations and coated as in Example 1 although it may be stored as fine material, preferably in a ventilated pile as described in the parent application. No external heat is applied at any time.

EXAMPLE 3

A product with the formula 0—14—15 containing about 2½% of chlorine may cheaply, quickly and easily be produced by the above process. To form the acidic sludge stir 880 pounds of potassium chloride with 1512 pounds of sulphuric acid (60° B. at 60° F.) for about 5 minutes. After about 300 pounds of hydrogen chloride gas has been evolved and removed, mix with 1325 pounds of phosphate rock. The evolved chlorine represents 75% of the total originally present. After the primary reaction is substantially complete form the mixture into discrete particles and promptly move them upon themselves until agglomerations with acid-wetted surfaces approaching the desired size are built up and coat them with 175 pounds additional of phosphate rock. Alternatively, the sludge may be mixed with 1440 pounds of phosphate rock and the product cured in said ventilated-pile, to give a fine cured product.

Alternatively potassium sulphate, finished or crude, may be mixed with the acid of usual concentration to form an acidic sludge which can be mixed with the fertilizer raw material,



with or without the addition of other sludges.

Another aspect of the processes herein is the employment of dolomite to furnish water-soluble magnesium, a product recommended by many agronomists for many types of soils preferably in combination with phosphates. In the above examples dolomite may well be substituted for at least a portion of the phosphate rock and/or as a coating for the pelleted product.

In connection with magnesium one must consider the question of water-solubility in its true meaning in connection with fertilizer base materials and ingredients.

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 in the solid, i.e. the dissolution is reversible. Water-extractability refers to the disappearance of certain or all the parts of a substance whether the liquid extract is a true solution of the original solid or not.

In conventional processes when ammonium hydroxide has been added to monocalcium phosphate in the presence of calcium sulphate the resulting products have been dicalcium phosphate and ammonium sulphate. Thus no water-soluble or water-extractable phosphatic product has resulted. When alkali metals, however have been combined with phosphorus to form acidic salts, truly water-soluble phosphates of these metals have been formed. Unlike conventional monocalcium phosphate, monomagnesium phosphate is soluble in water and hence has formed no problem when used alone or in combination only with phosphorus, as has been done successfully in the past. In ordinary superphosphate, however, soluble magnesium phosphate appears only in negligible quantities while water-extractable monocalcium phosphate is present in relatively large volume. Dolomitic limestone has been added to cured superphosphate to react with the free acid of the fertilizer and render additional quantities of magnesium water-soluble. If certain metals are present in sulphate form, this added dolomite will render them insoluble. If such metals are temporarily in an acid environment owing to the free acid and hence acid-soluble for the moment, they will be made insoluble by this neutralizing process. This process, however, makes it possible to produce a fertilizer in which magnesium, phosphorus, iron and other metals exist together in water-soluble and available forms. The value of such metals or "trace elements" in many soils is now widely recognized.

Dolomitic limestone is applied to certain soils to furnish, as it is slowly digested in the soil, magnesium and calcium hydroxide which change the pH balance of the soil and by substitution or replacement make otherwise fixed potassium therein assimilable by plants. This slow process is comparable to the direct application of phosphate rock to the soil. Magne-

sium salts applied as such to the soil hasten, often by years, the agronomic advantages secured from dolomitic limestone, but when prepared and used alone it is expensive. According to this process dolomitic limestone (like phosphate rock) is acidulated so that its benefits in full measure become almost immediately available. Moreover, the product hereof includes water-soluble magnesium phosphate. Magnesium in combination with phosphate, both in plant assimilable form, increase the value of each.

This phase is illustrated by a description of the production of a magnesium-potash base having 7% MgO and 25% K₂O of the latter of which approximately one-third is in the sulphate form and two-thirds in the chloride form. Ground dolomitic limestone and the above-described potash sludge of Example 3 are the base of this product. Dolomite contains up to 45% MgCO₃ and 55% of CaCO₃. An example follows:—

EXAMPLE 4

To form the acidic sludge, mix 1750 pounds of potassium chloride and an equal amount of sulphuric acid, 60° B. at 60° F., from 3 to 5 minutes. Where a dolomitic carbonate or hydroxide is used in place of ground phosphate rock, the amount is determined as that able to employ the acidic capacity of the sludge. The particular dolomite used in the above illustration has an "acid dolomite" factor of 1.15 which corresponds to an "acid rock" factor of 2.3 for the phosphate rock in the previous examples. In this case use 1650 pounds of ground dolomite.

If sufficient acidic potential is present, both the MgCO₃ and CaCO₃ are completely converted immediately, thereby forming a mixture of potassium, magnesium and calcium sulphate with no carbonates, but in the presence of insufficient acid for the complete conversion of both as above, the magnesium carbonate tends to decompose more rapidly than the calcium carbonate. Thus with insufficient acid for complete conversion more MgSO₄ is formed than CaSO₄. By mixing the above produced sludge and 1650 pounds of dolomite a net finished product after shrinkage of approximately 3200 pounds is secured. This product is granular, dry and free-flowing and can be shipped within a few hours after mixing although the solubility of the magnesium will slowly increase. If 300 pounds of the above raw materials are used in a short ton of fertilizer the product contains 1% of magnesium oxide and 3¾% of potash. The addition of 600 pounds of the above raw material to 1400 pounds of material containing nitrogen and phosphorus furnishes 2% of MgO together with slightly more than 7% of potash in a short ton of a complete fertilizer.

The acid may be mixed with the potassium chloride in a pan mixer. After the desired

amount of HCl has been removed the dolomite is added. This entire mixing operation is carried on for several minutes. The mixture of dolomite and acidic potassium sludge sets quickly but not in a hard mass. The greater the amount of potassium the more granular and free-flowing the mixture and hence the more readily it can be mixed. Other variants include the amount of acid relative to the solids to evolve the chlorine. After mixing, the mass is merely put through a sizing device and is ready for use, although solubility of the magnesium will continue to increase.

It has been discovered, furthermore, that this operation whether on a batch or continuous basis may be advantageously carried out by division of the ground limestone on the basis of particle size. Since dolomitic limestone varies from hard to soft, the fineness with which the material is ground adds greatly to the cost. It previously has been considered necessary to grind dolomitic limestone finely. By this process, however, good results are secured by relatively coarse grinding, for example so that 40% will not pass through a 100 mesh screen and 60% will pass through. First this coarse portion and all of the acid necessary to complete the acidulation are mixed. There must be sufficient liquid acid to reach all these coarse particles. After a few minutes of mixing so that the acid has had opportunity to reach the entire mass and begin the digestive process the finer particles are added.

EXAMPLE 5

In the following example of this phase of this invention 2650 pounds of potassium chloride are mixed with an equal amount of sulphuric acid of 60° B. Then add 2405 pounds of dolomite, 955 pounds in the first instance and the balance of 1445 pounds later, namely, a ratio of about 2 to 3.

Particularly since a relatively small amount of water-soluble magnesium is required for many complete fertilizers, one may employ dolomite in part and ground phosphate rock in part to make effective use of the acidulating potential of the sludge.

In processing such a mixed raw fertilizer material one may use the previously described ammonium sulphate sludge to produce a magnesium-nitrogen-phosphate product. The ammonium carbonate which may be formed by the double decomposition of the ammonium sulphate and magnesium of calcium carbonate, tends to decompose into NH_3 , CO_2 and H_2O , but this process is either retarded or stopped if monocalcium phosphate is present. The following illustration will make this clear:—

EXAMPLE 6

2000 pounds of ammonium sulphate sludge are mixed with 400 pounds of dolomite and 500 pounds of phosphate rock to yield a finished net product of approximately 2850

pounds which analyzes 10.1% N, 2.95% MgO and 5.75% P_2O_5 .

The above principles may also be applied to the making of a complete fertilizer including the potassium low-chlorine base with phosphate rock, acid and dolomite.

The following fertilizer will have a formula of 6—8—10 with 2% of MgO:—

EXAMPLE 7

In a pan mixer, stir 618 pounds of sulphuric acid of 60° B. and 335 pounds of potassium chloride for 3 to 5 minutes, thereby driving off 85 pounds of HCl. The resulting sludge has a net weight of 868 pounds. To this sludge, add 500 pounds of phosphate rock and 100 pounds of dolomite and, after rock, acid and dolomite have made thorough contact, 585 pounds of conventional dry sulphate of ammonia. Pour the mass into a den and remove it therefrom after it has set, disintegrate it and pass it into a pelleting drum. In a late stage of the pelleting operation coat with an additional 100 pounds of ground dolomite.

A further acidic sludge which may be used results from the acidulation of ground phosphate rock with sulphuric acid which has the advantage that dilute phosphoric acid may be separated from the resultant gypsum sludge as a by-product. This gypsum sludge which still contains free acid may be combined just as it comes from the phosphoric acid process either with other sludges or used independently to acidulate fertilizer raw materials as hereinbefore set forth.

This gypsum sludge is valuable since it carries sulphur and calcium, which are needed for many soils. In the frequent instances in which fertilizers with these elements as well as nitrogen, phosphorus and potash of moderate concentration of a lower grade are needed, fertilizer raw materials are mixed with this gypsum phosphorus-bearing sludge while still moist, permitted to stand for a few minutes and disintegrated. Then the mass is moved upon itself to form agglomerations and coated as previously described. Almost all of the available phosphorus contained in the gypsum is thereby utilized.

This gypsum sludge makes possible a dry and pelleted product by the use of certain fertilizer ingredients which otherwise could not be handled readily. In the example which follows the phosphate rock performs the dual function of providing the fertilizer raw material to be digested and providing the finely divided coating material for the pellets.

EXAMPLE 8

A product of an analysis of 10—2—14 is made from 975 pounds of ordinary commercial sulphate of ammonia, 500 pounds of ordinary potassium chloride, 550 pounds of gypsum sludge of 3.2% P_2O_5 , and 75 pounds of ground phosphate rock, this amount of





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ingredient, said fertilizer
ingredient, fertilizer

coating material being slightly less than the usual 5% because of the slightly lowered moisture and free acid content of the mass. The ingredients other than the phosphate rock are mixed in an ordinary mixing pan and passed to a pelleting drum or its equivalent wherein it is moved upon itself and in a late stage of the agglomeration operation the phosphate rock is added as a coating. The result is a dry, free-flowing homogeneous pellet composed largely of nitrogen and potash but having enough phosphorus for many fertilizer purposes.

EXAMPLE 9

Such a phosphorus-bearing gypsum sludge is used for making a fertilizer useful for certain soils where gypsum is highly desirable but little phosphorus is needed. A complete fertilizer answering this need of an analysis of 6—5—6 is made by mixing 900 pounds of gypsum sludge having 3.2% of P_2O_5 , 200 pounds of potassium chloride, 675 pounds of sulphate of ammonia sludge prepared as above and containing 17.8% of nitrogen, and 125 pounds of ground phosphate rock of 72% bone phosphate of lime. After preliminary mixing these materials are passed through a pelleting drum or otherwise agitated to form agglomerations, which are then coated with an additional 100 pounds of phosphate rock, thereby using a total of 225 pounds.

Alternatively, particularly when a low-grade fertilizer is wanted together with calcium and/or sulphur, commercial gypsum or a gypsum sludge without an acidic potential may be used in combination with another acidic sludge.

WHAT I CLAIM IS:—

1. 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 solid fertilizer raw material is reacted with a preponderantly dry acidic sludge which contains the inorganic acid material together with a 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.

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

3. A process according to Claim 1 or 2, wherein said solid fertilizer raw material is ground phosphate rock or other phosphatic ore and/or ground dolomitic limestone.

4. A process according to any one of the preceding claims, and including the step of preforming the acidic sludge by reacting a precursor of the fertilizer ingredient with an excess of the inorganic acid material.

5. A process according to Claim 4, wherein said sludge is formed by absorbing ammonia in relatively concentrated sulphuric acid and carrying said absorption past the point at which solid ammonium sulphate separates.

6. A process according to Claim 4, wherein said sludge is prepared by reacting potassium chloride and sulphuric acid.

7. A process according to Claim 4, wherein said sludge is preformed by digesting phosphate ore by sulphuric acid and removing a dilute solution of phosphoric acid as a by-product.

8. A mixed fertilizer when prepared by a process as claimed in any one of the preceding claims.

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*ingredient, said fertilizer
ingredient, fertilizer*

coating material being slightly less than the usual 5% because of the slightly lowered moisture and free acid content of the mass. The ingredients other than the phosphate rock are mixed in an ordinary mixing pan and passed to a pelleting drum or its equivalent wherein it is moved upon itself and in a late stage of the agglomeration operation the phosphate rock is added as a coating. The result is a dry, free-flowing homogeneous pellet composed largely of nitrogen and potash but having enough phosphorus for many fertilizer purposes.

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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 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.

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

3. A process according to Claim 1 or 2, wherein said solid fertilizer raw material is ground phosphate rock or other phosphatic ore and/or ground dolomitic limestone.

4. A process according to any one of the preceding claims, and including the step of preforming the acidic sludge by reacting a precursor of the fertilizer ingredient with an excess of the inorganic acid material.

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* C L M S *