

June 3, 1958

J. E. SEYMOUR

2,837,418

PROCESSES FOR PRODUCING MIXED FERTILIZERS

Filed March 29, 1955

3 Sheets-Sheet 1

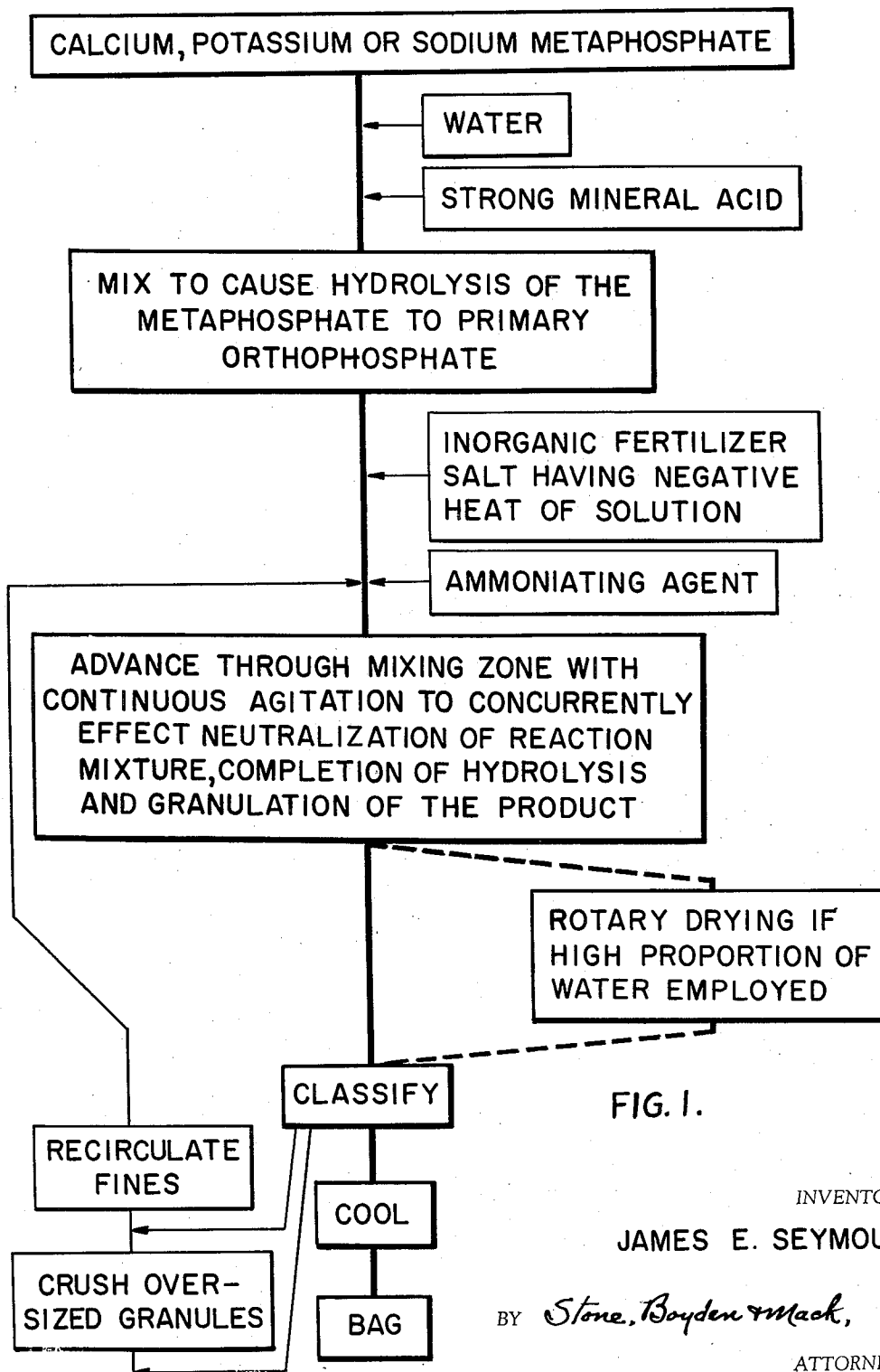


FIG. 1.

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3 Sheets-Sheet 2

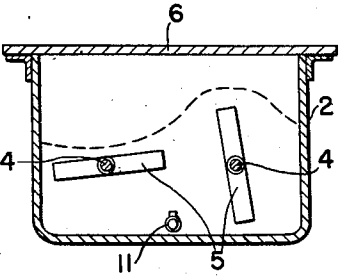
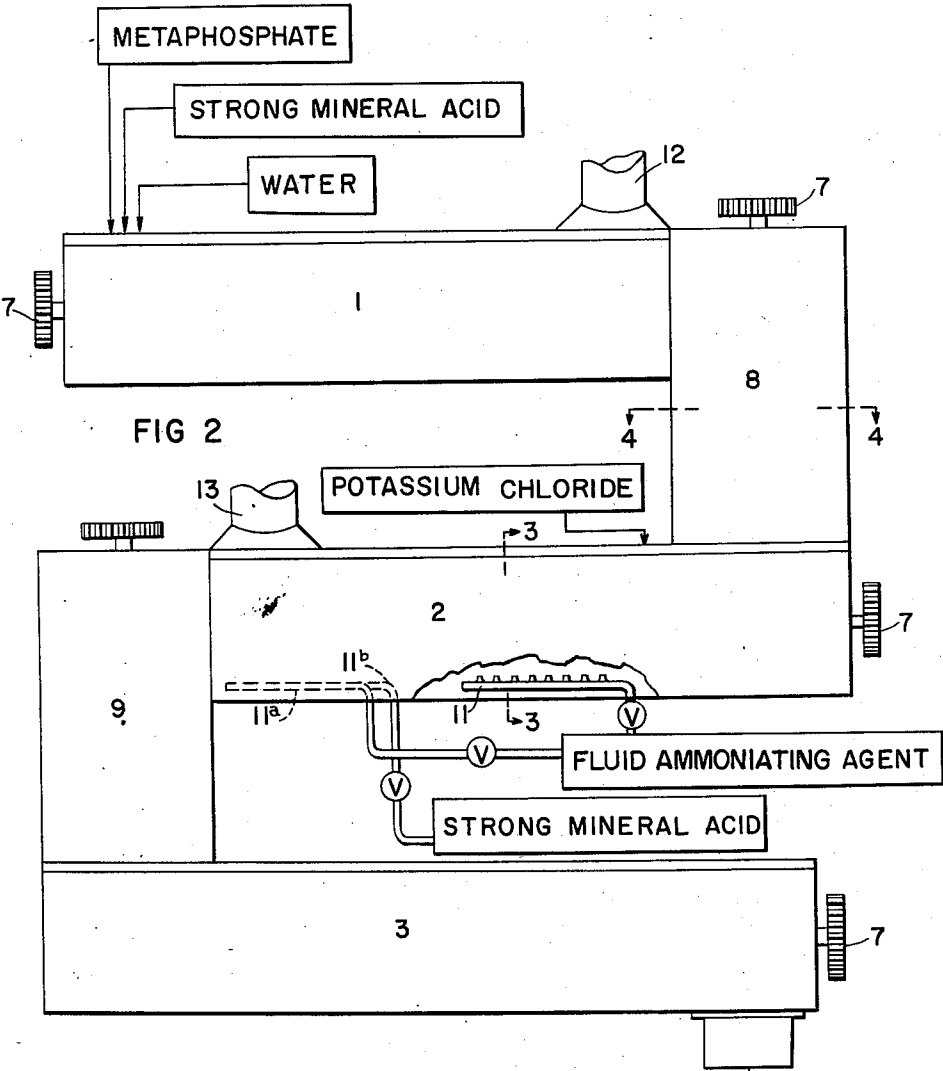


FIG 3

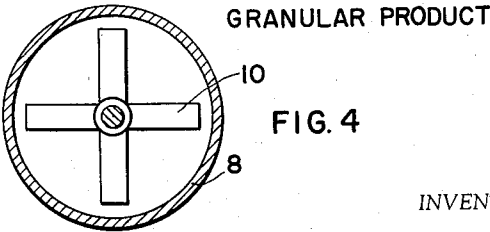


FIG. 4

GRANULAR PRODUCT

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FIG. 5

EXAMPLE	PARTS BY WEIGHT										% AVAILABILITY OF PRODUCT			RATIO OF ACID TO METAPHOSPHATE
	CaPO_3	KPO_3	NaPO_3	95.5% H_2SO_4	38% HCl	70% HNO_3	75% H_3PO_4	H_2O	AMMONIATING AGENT		N	P_2O_5	K_2O	
5	68.30			7.60				13.00	SOLUTION "D" 11.10		5.5	43.5		0.1
6	29.70			46.50				5.90	17.90		14.5	19.0		1.5
7	69.57				18.31			2.56	SOLUTION "D" 9.56		4.7	44.5		0.1
8	72.50					10.36		11.38	SOLUTION "D" 5.76		4.5	46.5		0.1
9	28.21					60.38			ANHYDROUS NH_3 11.41		21.0	20.5		1.5
10	74.07						98.7	12.36	SOLUTION "D" 3.70		1.8	52.7		0.1
11	29.37						58.73		ANHYDROUS NH_3 11.90		10.6	20.4		1.5
12		69.57			18.31			2.56	SOLUTION "D" 9.56		4.7	44.9	27.8	0.1
13		35.01				26.69		10.50	SOLUTION "D" 27.8		20.0	23.6	15.7	0.5
14		29.37					58.73		ANHYDROUS NH_3 11.90		10.6	19.1	12.7	1.5
15			69.57		18.31			2.56	SOLUTION "D" 9.56		4.7	44.9		.1
16			28.21			60.38			ANHYDROUS NH_3 11.41		21.0	20.7		1.5
17			29.37				58.73		ANHYDROUS NH_3 11.90		10.6	20.6		1.5

NOTE: SOLUTION "D" CONSISTS OF 34% ANHYDROUS AMMONIA, 60% AMMONIUM NITRATE AND 6% WATER.

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PROCESSES FOR PRODUCING MIXED FERTILIZERS

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Application March 29, 1955, Serial No. 497,785

9 Claims. (Cl. 71—64)

This invention relates to an improved process for manufacturing mixed fertilizers and is a continuation-in-part of my copending application, Serial Number 267,833, filed January 23, 1952, now abandoned.

According to present commercial practice, N-P and N-P-K fertilizers are usually produced by ammoniating superphosphate with or without the addition of a potassic ingredient. In some processes, the ammoniation step is integrated into the well known process for producing calcium superphosphate by acidulation of phosphate rock. In others, superphosphate which has been cured is ammoniated in a separate process. In either case, the common commercial practice requires the production of calcium superphosphate from phosphate rock by acidulation.

Such processes have several severe disadvantages. In general, the conventional acidulation of phosphate rock is not a very desirable commercial process since it requires a cumbersome and expensive plant, employs large quantities of acid relative to the available phosphorous content of the product, and is not very flexible insofar as production of the various different grades of fertilizers required by the trade is concerned. The product of the acidulation process usually must be cured for prolonged periods in order to assure completion of the reactions between the acid and phosphate rock, and such curing results in the formation of substantially solid masses of superphosphate which must be broken up, often by dynamiting. This creates an undue delay in time, and usually results in a severe dust problem which endangers the health of the workers and decreases efficiency of the plant. Conventional processes for ammoniating the superphosphates from such procedures have not been entirely successful. It has been difficult to carry out the ammoniation reaction and no completely satisfactory process equipment for this has apparently yet been devised. Further, an ammoniated product is not of satisfactory condition and requires a separate treatment for granulation.

A general object of the present invention is provision of an improved process for producing mixed fertilizers whereby the disadvantages just discussed are largely overcome.

Another object is the production of novel mixed fertilizer products of greatly improved physical condition.

A further object is to devise a relatively simple process for producing mixed fertilizers, either in batch or as a continuous procedure, in such a manner that the product is substantially dry, completely reacted and fully granulated so that no separate granulating or curing steps are required. In this connection, my process provides for the manufacture of complete mixed fertilizers in such a manner that the procedure need not be interrupted from the time the raw materials are combined until the completed product is charged into packages for sale.

Yet another object is to provide a fertilizer process

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requiring less acid per unit of available fertilizer material in the product and capable of producing products of unusually higher analysis.

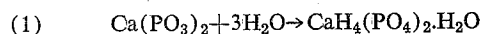
Still another object is provision of a process for producing fertilizers containing available nitrogen and phosphorous in relatively high proportion with accurate predetermination of the N:P ratio of the product. In this connection, my improved process may be said to be very flexible in that it is adapted to produce the widely varying grades of mixed fertilizers now in demand.

A further object of the invention is to provide such a process including a novel ammoniation procedure whereby the temperature rise in the reaction mixture during ammoniation is reduced.

In general, I accomplish these results by employing a metaphosphate selected from the group consisting of calcium metaphosphate, potassium metaphosphate and sodium metaphosphate, hydrolyzing the metaphosphate in the presence of a strong mineral acid as a hydrolyzing agent or catalyst, so that the metaphosphate is converted to the corresponding primary orthophosphate, which in turn may be partially or completely acidulated by the acid, and substantially completely neutralizing the resulting reaction mixture by means of an ammoniating agent.

The metaphosphates themselves are well known as fertilizer materials for direct application to the soil, and it is recognized that when so applied the metaphosphates will gradually hydrolyze. It has also long been known that the metaphosphates may be hydrolyzed by boiling in water for prolonged periods, or by contacting with water and phosphoric acid at high temperatures in the molten state, in which latter case hydrolysis proceeds rapidly. Hydrolysis by such methods is not, however, suitable for commercial production of fertilizers because, on the one hand, of the time involved and, on the other hand, of the excessively high starting temperatures and adverse process conditions.

I have discovered that the metaphosphates referred to may be hydrolyzed to the corresponding primary orthophosphate rapidly, in a period of from a few seconds to a few minutes, by a procedure ideally adapted for commercial fertilizer plant operation. To accomplish this, I contact the metaphosphate with water and strong mineral acid to form a slurry in which the proportion of water is sufficient for substantial hydrolysis of the metaphosphate but does not exceed about five times the stoichiometric amount necessary for complete hydrolysis, and in which the acid-to-metaphosphate weight ratio is in the range of 0.1-1.5. The hydrolysis reaction, once initiated, is exothermic and proceeds rapidly in accordance with the following equation:



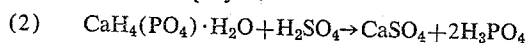
When the stoichiometric proportion of water necessary for complete hydrolysis is present, the reaction will go rapidly to completion once it is initiated, so that substantially all of the metaphosphate is converted quickly to the corresponding primary orthophosphate. Though prior work with the metaphosphates had indicated that the hydrolysis must be either slow or at high initial temperature, I have discovered that the use of a strong mineral acid in the proportions herein stated allows my process to start at low temperatures and yet obtain a satisfactory reaction rate. Thus, when sulfuric acid is employed in accordance with the invention, substantially complete hydrolysis of the metaphosphate is effected in a mixing period of from 15 seconds to about 5 minutes. When calcium metaphosphate is employed with the other strong

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mineral acids (hydrochloric, nitric or phosphoric), the hydrolysis reaction is materially slower. Even here, however, the mixing time just mentioned is effective to initiate hydrolysis and carry the same on to a very material extent, the reaction then being very rapidly completed when the temperature of the reaction mixture is raised during ammoniation. Potassium metaphosphate and sodium metaphosphate hydrolyze rapidly with sulfuric, hydrochloric, nitric or phosphoric acid under the conditions of the process and the hydrolysis can be carried substantially to completion before ammoniation simply by mixing for the relatively short period above mentioned.

It is not necessary to carry hydrolysis to completion before ammoniation, since the hydrolysis will be effected during ammoniation so long as the proportion of acid and water specified above are employed. In all events, however, it is necessary to carry out a preliminary mixing step not only to initiate hydrolysis but also to assure intimate contact between the metaphosphate, water and acid.

The strong mineral acid does not itself enter into the hydrolysis reaction. When sulfuric, hydrochloric or nitric acid is employed, the original acid reacts with the primary orthophosphate resulting from hydrolysis, producing phosphoric acid. Thus, either the original acid, or the phosphoric acid produced by acidulation, or both, is available for reaction with the ammoniating agent employed to neutralize the reaction mixture. Further, if sulfuric acid is employed as the hydrolyzing agent, two moles of phosphoric acid will be produced for each mole of sulfuric acid employed.



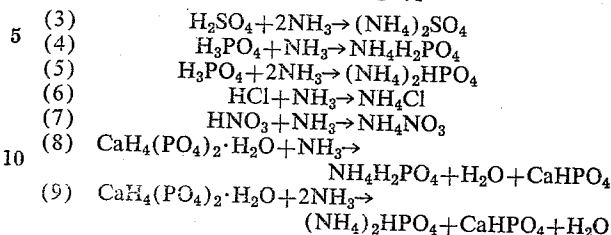
It will thus be noted that the hydrolysis and acidulation reactions run concurrently. While the original acid is progressively destroyed, I have discovered that this has no material disadvantageous effect on the hydrolysis reaction. It should also be noted that it is possible to employ either more or less than the stoichiometric proportion of sulfuric, hydrochloric or nitric acid required for reaction with the primary orthophosphate which results from complete hydrolysis of the metaphosphate. Therefore, I am able to convert either all or only a portion of the primary orthophosphate to phosphoric acid.

Accordingly, by the concurrent hydrolysis and acidulation reactions with sulfuric, hydrochloric or nitric acid as a starting material, I am able to (1) produce the primary orthophosphate without using up acid, and (2) produce from the orthophosphate a desired amount, within a wide range, of phosphoric acid, using for this purpose the same acid employed as the catalyst for hydrolysis and gaining a yield of two moles of phosphoric acid for each mole of sulfuric acid employed when the latter is the hydrolyzing agent used.

Employing adequate water for substantially complete hydrolysis of the metaphosphate, and preferably a slight excess to assure complete hydrolysis, the combination of water, metaphosphate and acid is a relatively thick slurry which may be readily handled in conventional propeller type mixers, pug mills, etc. As the hydrolysis and acidulation reactions proceed to completion, the slurry is converted to a somewhat stiffer pasty mass which is still readily handled by such devices. I have discovered that if this reaction product is neutralized with an agent providing neutralizing ammonia, and if the reaction mixture is continually mixed during such neutralization, the mixture is quickly converted to a fully granular, substantially dry fertilizer product. I may employ for this purpose any suitable ammoniating agent providing neutralizing ammonia, of which I prefer anhydrous ammonia, ammonium hydroxide solution, ammonium nitrate-anhydrous ammonia solution, urea-ammonium hydroxide solutions or urea formaldehyde-ammonium hydroxide solutions. It will be noted that, aside from the sulfate result-

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ing from the acidulation reaction, all of the products of the hydrolysis and acidulation reactions are ammoniatable, as indicated by the following typical reactions:



As has been pointed out, the amount of phosphoric acid produced as a result of acidulation of the orthophosphate can be predetermined by proper choice of the proportion of sulfuric acid within the range stated. Thus, if a product having a higher proportion of nitrogen is desired, I employ more sulfuric, hydrochloric or nitric acid so as to produce a greater amount of phosphoric acid to react with the ammoniating agent. If phosphoric acid is employed as the hydrolyzing agent, the proportion of this acid used may be increased above that amount necessary to promote hydrolysis, so providing for greater ammoniation and a higher proportion of nitrogen in the product. On the other hand, if a product having less available nitrogen in proportion to the available phosphorous is desired, I may employ less acid, so that there is less phosphoric acid available for ammoniation. In either event, it is desirable to employ adequate ammoniating agent to substantially completely neutralize the acid constituents of the reaction mixture. While a slight excess of ammoniating agent will ordinarily be employed, a slightly acidic product is sometimes permissible.

Conversion of the reaction mixture to a granular finished product is surprisingly abrupt in comparison to conventional processes. Thus, as will be hereinafter explained, the conversion from slurry or paste form at the ammoniation point to a granular product occurs within as little as 6" of travel of the reaction mixture through a pug mill. It appears that such action is due at least in part to the fact that, at the time of ammoniation, the reaction mixture has a relatively high, uniformly distributed, liquid content, with the result that the products of ammoniation tend to form as a crystalline mass which is broken up into granules and agglomerated by the mixing or stirring action. The reactions involved in my process are rapid and exothermic, and go quickly to completion, so that curing is unnecessary. The heat generated, when the proportions specified are employed, is adequate to drive off the excess water present, except when the higher proportions of water are employed. Accordingly, I am able to cool the product directly after ammoniation and charge it into packages without interrupting the operation.

The neutralization of a reaction mixture comprising acid fertilizer materials by means of ammoniation agents providing free or neutralizing ammonia results in the evolution of considerable heat. This is undesirable because the other reactions involved in my process are strongly exothermic, because it is more convenient if the product can be quickly cooled, and because at high temperatures there may be some tendency for the phosphorous content of the product to revert to the unavailable form. In order to reduce the reaction temperature at the time of ammoniation, I prefer to employ, substantially simultaneously with ammoniation, an additional inorganic fertilizer salt which has a negative heat of solution in the reaction mixture. Thus, I may employ as the additional salt potassium chloride, potassium sulfate, ammonium nitrate or ammonium sulfate. Since the reaction mixture obtained in my process prior to ammoniation has a considerable liquid content, the additional fertilizer salt is dissolved with the absorption of considerable heat. Therefore, if the additional fertilizer

salt is incorporated in the reaction mixture with agitation shortly before, or at the same time as, or immediately after ammoniation, a material portion of the heat generated by the ammoniation reactions will be absorbed by reason of the negative heat of solution of such additional ingredient.

A typical illustrative flow sheet, based on calcium metaphosphate as the starting material, is given in Fig. 1. Here, it will be noted that the product is classified before cooling and bagging, the fines being recirculated to the process substantially at the point of ammoniation to increase the surface area of the solids at this point.

If desired, the process may be carried out "in batch" in any suitable batch type mixer. But, I find it advantageous to employ a continuous procedure in which the raw materials are continuously introduced into an elongated mixing zone and the granular product is continually delivered from the discharge end of the zone. With such a method, I may employ part of the mixing zone to cool the product, so that the cooled product may be delivered directly to bags. In order that the continuous embodiment of my process may be understood in more detail, an illustrative apparatus is shown diagrammatically in Figs. 2-4, of which:

Fig. 2 is a diagram of the apparatus in side elevation;

Fig. 3 is a vertical sectional view taken on line 3-3, Fig. 2, and

Fig. 4 is a vertical sectional view taken on line 4-4, Fig. 2.

As seen in Fig. 2, the apparatus employed is in the nature of a 3-tiered double pug mill having an upper tier 1, an intermediate tier 2 and a lower tier 3. As seen in Fig. 3, each tier of the mill is provided with two parallel shafts 4 carrying longitudinally spaced pug mill blades 5. Each tier of the pug is provided with a sealed cover 6. The shafts 4 are counter-rotated by any suitable means, as by gears 7. The tiers 1-3 are connected by vertical sections 8 and 9 which, as seen in Fig. 4, are equipped with rotary agitators 10.

A reaction slurry is established at the start of tier 1 by feeding in the metaphosphate, acid and water continuously in the proper proportions. The rates of feed are selected so that the reaction mixture bed being handled by the pug mill is of considerable depth, as indicated in Fig. 3. The counter-rotating pug mill blades 5 advance the slurry continuously along the tiers with continuous, vigorous agitation.

At a point immediately after delivery of the reaction mixture to the intermediate tier 2, potassium chloride or other suitable fertilizer salt having a negative heat of solution in the reaction mixture, is added. An ammoniating fluid spray pipe 11 is situated in the bottom of the tier 2 at this point, as shown in Figs. 2 and 3. The spray pipe 11 is aligned with the direction of travel of the reaction mixture and is positioned with its spray apertures or nozzles, which are longitudinally spaced on the pipe, directed upwardly, so that fluid ammoniating agent supplied to the pipe 11 under pressure is injected from below upwardly into the bed of reaction mixture. A second spray pipe 11^a is provided, the second pipe being located at a point in tier 2 downstream from pipe 11 by a distance (usually 18-24 inches) sufficient to allow complete neutralization and granulation of the initial product. Positioned beside pipe 11^a is a third spray pipe 11^b connected to a suitable supply of strong mineral acid.

Fumes are taken off via flues 12 and 13, one located at the end of the preliminary mixing zone and the other at the end of the ammoniation zone.

Figs. 2-4 illustrate diagrammatically the essential features of a pilot plant in which the present invention has been carried out and will be referred to in certain of the examples hereinafter.

As has been indicated, mixing of the metaphosphate, acid and water in the proportions defined provides a

slurry and mixing of the slurry effects hydrolysis. With tiers 1-3 each approximately 4 feet long and with rotary blades 5 operating to advance the reaction mixture at 2-8 feet per minute, hydrolysis of the metaphosphate will always be carried to a considerable extent in tier 1. If sulfuric acid and calcium metaphosphate are employed, and the water is not more than twice the amount required for hydrolysis, the hydrolysis will be complete in tier 1. If calcium metaphosphate is employed with phosphoric, hydrochloric or nitric acid, the hydrolysis will be correspondingly slower in tier 1, but will be completed in the ammoniation zone of tier 2. Hydrolysis of potassium and sodium metaphosphate can readily be made complete in tier 1 with any of the four acids.

Assuming the use of "cold" acid, the reaction mixture at the end of tier 1 will ordinarily be in the range of 100-350° F., assuming that ambient temperature is room temperature. The hydrolysis reaction temperature depends upon the particular acid employed, the amount of water, the particle size of the metaphosphate and the acid-to-metaphosphate ratio.

It will be understood that, depending upon the grade of product desired, it is not necessary that hydrolysis be predominantly completed prior to ammoniation. The fact that the extent of hydrolysis can be readily controlled in the mixing zone prior to ammoniation enables me to select the physical condition of the reaction mixture and the temperature thereof as the reaction mixture enters the ammoniation zone. Such control is highly desirable.

In actual practice, I find it is advantageous to effect extensive hydrolysis of the metaphosphate in the mixing zone of tier 1, the reaction temperatures before ammoniation therefore being relatively high. While such high temperatures are a favorable condition in hydrolysis, it is not desirable to commence ammoniation at excessive temperatures. I therefore lower the temperature of the reaction mixture by adding the potassium chloride, or other fertilizer salt having a negative heat of solution, substantially at the point of ammoniation. If desired, some of the water employed may be sprayed in at this point.

Ammoniation can also be improved by recirculating product fines to the process at the ammoniation point so as to increase the surface areas of the solids.

Ammoniation has always been a difficult step in the fertilizer industry because of the high ammonia losses normally encountered. I find that ammoniation in my process can be greatly improved because of the physical condition of the reaction mixture and because the ammoniation reactions are completed in an unusually short time. Because the reaction mixture is in the form of a thick slurry or a pasty mass at the time ammonia is added, I am able to inject ammonia into the reaction mixture from below, so that the tendency for the ammonia to escape is greatly reduced. As ammoniation occurs, the mixing and shearing action of the pug mill blades immediately granulates the product.

The following examples are illustrative:

Example 1

	Parts by weight
Calcium metaphosphate	59.4
Sulfuric acid (95.5%)	26.6
Water	14.0

The reactants were combined in a bowl type mixer at room temperature and continuously mixed for 30 seconds. In that period the reaction mixture changed to a pasty mass and a reaction temperature of approximately 320° F. was obtained. While mixing continued, ammonium hydroxide solution (28% NH₃) was added in slight excess of the amount which would react with the acid constituents of the slurry, this being accomplished by injecting the ammoniation solution into the lower portion of the reaction mixture. Mixing was then continued for an

additional two minutes, at the end of which time the product was fully granular. One day after manufacture, the product analyzed 18.5% nitrogen, 26.35% total P_2O_5 and 26.15% available P_2O_5 . Basicity to methyl orange as NaOH was 4.8. The acid-to-metaphosphate weight ratio in the initial slurry was 0.42.

Example 2

	Parts by weight
Potassium metaphosphate-----	63.7
Sulfuric acid (95.5%)-----	26.5
Water-----	9.8

The procedure was the same as in Example 1, except that urea-ammonia solution (45.5% N) was employed as the ammoniating agent. Maximum reaction temperature was 200° F. Four days after manufacture, the product analyzed 17.98% nitrogen, 29.6% available P_2O_5 and 18.95% potash as K_2O . The pH was 7.2. The product was dry in appearance, fully granular, and water soluble. The acid-to-metaphosphate weight ratio was .397 in the original slurry.

Example 3

	Parts by weight
Sodium metaphosphate-----	50.2
Sulfuric acid (95.5%)-----	25.3
Water-----	7.7

The procedure is the same as in Example 1, using 16.8 parts by weight anhydrous ammonia as the ammoniating agent. The product is dry, fully granulated, and analyses 14% nitrogen and 35% available P_2O_5 . The acid-to-metaphosphate weight ratio in the original slurry is 0.48 and the maximum reaction temperature 210° F.

Example 4

In order to illustrate the process broadly when a potassic ingredient is employed to produce a 1-1-1 product, a slurry was prepared in a bowl mixer by combining:

	Parts by weight
Calcium metaphosphate-----	21.80
Sulfuric acid (60° Bé.)-----	15.28
Water-----	2.70

The acid-to-metaphosphate weight ratio was 0.544. The slurry was mixed for 30 seconds, in which time a reaction temperature of about 280° F. was attained and the reaction mixture changed to a pasty mass. To this mass was then added 22.47 parts by weight potassium chloride (62% K_2O) with continual mixing for an additional 30 seconds. The reaction mixture was then fully ammoniated by injecting into the mixture 37.75 parts by weight of an ammoniating solution consisting of 16.6% anhydrous ammonia, 16.6% water and 66.8% ammonium nitrate. Mixing was continued for 2 minutes after introduction of the ammoniating solution, the product being converted to fully granular form. Two days after manufacture, the product analyzed:

	Percent
Moisture-----	2.30
Total nitrogen-----	14.68
Total P_2O_5 -----	15.10
Citrate insoluble P_2O_5 -----	.15
Available P_2O_5 -----	14.95
Potash as K_2O -----	14.42
Basicity to Methyl Orange as NaOH-----	2.20

For purposes of simplicity, additional examples are tabulated in Fig. 5 to illustrate the operability of the process with other metaphosphates and acids. All examples in Fig. 5 are based upon laboratory scale, bowl-mixer operations, as in Examples 1-4.

The following examples are taken from pilot plant operation with apparatus essentially as in Figs. 2-4;

Example 18

A 13-13-13 product was produced in apparatus having

the characteristic features illustrated in Figs. 2-4. Calcium metaphosphate, sulfuric acid and water were fed continuously to the upstream end of the first tier of the pug mill at rates providing the following proportions:

	Parts by weight
Calcium metaphosphate-----	100.0
Sulfuric acid (60° Bé.)-----	63.9
Water-----	12.0

10 The mixture advanced along the first tier of the pug mill as a thickening slurry, passing to the second tier as a pasty mass. Temperature of the reaction mixture in the latter stage of the first tier was 270-300° F. Time of travel was approximately one minute.

15 An intimate mixture of potassium chloride and ammonium sulfate was incorporated in the reaction mixture by feeding continuously to the entrance end of the second tier at a rate providing:

	Parts by weight
20 Potassium chloride-----	105.0
Ammonium sulfate-----	120.0

At a point in the second tier immediately downstream from the point of addition of the potassium chloride-ammonium sulfate mixture, a liquid ammoniating agent was injected into the reaction mixture from below by a spray pipe arranged as illustrated at 11, Figs. 2 and 3. The ammoniating agent was fed at a rate providing a proportion of 79.5 parts by weight ammoniating solution. The ammoniating solution consisted of 34% anhydrous ammonia, 60% ammonium nitrate and 6% water. Temperature of the reaction mixture in the ammoniating zone was 180-220° F. The product was fully granular within 12" of travel after the first introduction of ammoniating agent. The product delivered directly from the pug mill was substantially dust free, with 85% of the granules being less than 4 mesh. Analysis of the product 2 days after manufacture was:

	Percent
40 Moisture-----	.76
Total nitrogen-----	13.05
NH ₃ nitrogen-----	11.10
NO ₃ nitrogen-----	1.95
Total P_2O_5 -----	13.75
45 Citrate insoluble P_2O_5 -----	.20
Available P_2O_5 -----	13.55
Potash as K_2O -----	13.07
Basicity to Methyl Orange as NaOH-----	.30

50 The formulation was for a 13-13-13 product. The analysis indicates that hydrolysis of the metaphosphate, acidulation of the monocalcium orthophosphate, and neutralization of the product, were all substantially complete.

The product consisted of very hard, peach colored granules which were homogeneous as to constituency. The 85% which passed through a 4 mesh screen was predominately larger than 20 mesh and smaller than 6 mesh. The product was of such condition that it could be bagged immediately after screening and cooling.

Example 19

A 20-20-20 product is prepared by continuously feeding potassium metaphosphate, nitric acid and water to the entrance end of the first tier of the pug mill at rates sufficient to provide:

	Parts by weight
Potassium metaphosphate-----	33.33
Nitric acid (70%)-----	25.41
Water-----	10.00

70 While mixing of the resulting slurry in the first tier results in at least as rapid a hydrolysis as in Example 18, the temperature of the reaction mixture delivered to the second tier is somewhat lower.

An intimate blend of potassium chloride and solid urea is fed to the entrance end of the second tier of the

pug mill at a rate incorporating these ingredients in the reaction mixture in the following proportions:

	Parts by weight
Potassium chloride-----	11.12
Urea -----	22.02

Immediately downstream of such addition, 7.47 parts by weight of anhydrous ammonia is injected into the reaction mixture in the same manner described in Example 18. The reaction mixture again becomes fully granular within 12-18" of travel after ammoniation.

Example 20

A 1-4-4 product was prepared in the following manner: Calcium metaphosphate, sulfuric acid and water were fed to the intake of the first pug mill tier at rates providing:

	Parts by weight
Calcium metaphosphate-----	35.50
Sulfuric acid (60° Bé.)-----	10.00
Water -----	5.25

The slurry was passed through the first tier in about one minute, increased materially in thickness, and attained a temperature of 250-270° F.

Potassium chloride was continuously fed to the intake of the second tier at a rate providing 37.5 parts by weight in the reaction mixture. At a point immediately following such addition, a liquid ammoniating solution was added, in the manner described in Example 18, at a rate providing 11.75 parts by weight in the reaction mixture. The ammoniation solution consisted of 34% anhydrous ammonia, 60% ammonium nitrate and 6% water. The temperature in the ammoniation zone was 180-220° F.

The product was fully granulated in 18" of travel beyond the ammoniation point. One day after manufacture, the product analyzed:

	Percent
Moisture -----	3.35
Total nitrogen-----	6.05
NH ₃ nitrogen-----	4.23
Total P ₂ O ₅ -----	23.90
Citrate insoluble P ₂ O ₅ -----	.45
Available P ₂ O ₅ -----	23.45
Potash as K ₂ O-----	22.94
Acidity to Methyl Orange as NaOH-----	.20

In referring to Figs. 2-4, it was pointed out that a secondary ammoniation step could be carried out, injecting the additional ammoniating agent via pipe 11^a and employing additional acid at this point. The following example is typical:

Example 21

Calcium metaphosphate, sulfuric acid and water are supplied continuously to the intake of the first tier of the pug mill to provide:

	Parts by weight
Calcium metaphosphate-----	22.25
Sulfuric acid (60° Bé.)-----	14.25
Water -----	3.00

With a time of travel of one minute in the first tier, the metaphosphate hydrolysis and acidulation of the monocalcium orthophosphate are substantially complete when the reaction material enters the second tier. Potassium chloride is fed continuously to the intake of the second tier to provide 23.50 parts by weight in the reaction mixture. The same ammoniating solution employed in Example 20 is injected immediately after addition of the potassium chloride (as by pipe 11, Fig. 2). In 18" of travel, the product is completely granular.

At a down-stream point in the second tier (as by pipes 11^a and 11^b), additional quantities of sulfuric acid and the ammoniating solution are continuously injected simultaneously into the agitated flowing bed of granular prod-

uct to provide 15.45 parts by weight additional 60° Bé. sulfuric acid and 12.00 parts by weight additional ammoniating solution. The additional acid and ammoniating solution react to form ammonium sulfate which, along with the ammonium nitrate of the solution, deposit as a coating upon the granules of the product. The resulting product analyzes approximately 14-14-14.

In the foregoing examples, the metaphosphate employed is particulate, not exceeding 8 mesh. Rapidity of hydrolysis increases with decreasing particle size, and excellent results are obtained with a metaphosphate of predominantly 35 mesh.

For simplicity, the examples have each employed only a single acid and a single metaphosphate. It will be understood that combinations of the metaphosphates may be employed and that combinations of the acids may be employed. Thus, if a given potash content is desired in the finished product, calcium metaphosphate may be supplemented with potassium metaphosphate. While it is usually desirable to depend upon the heat of ammoniation to complete hydrolysis in cases where unhydrolyzed calcium metaphosphate remains at the end of the preliminary mixing step, it will be understood that heat may be supplied to the initiated slurry if desired. In some cases, heat may be supplied by using warm acid, hot water or steam. I have found that, when sulfuric acid is employed, it is desirable to employ an aqueous acid solution and separately added water, keeping the added water in the range of 20-60% of the combined weight of the aqueous acid and added water. When this is done, the greatest possible heat of solution of the sulfuric acid is obtained during initial mixing of the slurry, and the rate of hydrolysis is correspondingly increased. This is characteristic of sulfuric examples given hereinbefore.

I claim:

1. A self-granulating process for producing high analysis mixed fertilizers comprising the steps of (1) combining at least one particulate metaphosphate selected from the group consisting of calcium metaphosphate, potassium metaphosphate and sodium metaphosphate with water and at least one strong mineral acid selected from the group consisting of hydrochloric acid, nitric acid, phosphoric acid and sulfuric acid to provide a reaction mixture in the form of a slurry, (2) intimately mixing said reaction mixture and thereby initiating hydrolysis of the metaphosphate with such hydrolysis progressing exothermically as mixing continues, (3) then incorporating neutralizing ammonia in said reaction mixture in proportion for substantially complete neutralization of the acid constituents of the reaction mixture, and (4) then further intimately mixing said reaction mixture as said neutralizing ammonia reacts with said acid constituents and, by such further mixing, causing the reaction mixture to be converted to a substantially fully reacted fertilizer product in the form of solid granules which are substantially homogeneous as to chemical constituency, the proportion of acid employed being in the range of from 0.1 to 1.5 parts by weight per part by weight of said metaphosphate, and the proportion of water employed being 1-5 times the stoichiometric quantity required for complete hydrolysis of the metaphosphate.

2. The process of claim 1 wherein the acid employed is sulfuric acid, and intimate mixing of the reaction mixture in step (2) effects not only initiation of hydrolysis of the metaphosphate but also acidulation of the products of hydrolysis with resultant formation of phosphoric acid as a constituent of the reaction mixture.

3. A continuous, self-granulating process for producing high analysis mixed fertilizers comprising the steps of (1) combining at least one particulate metaphosphate selected from the group consisting of calcium metaphosphate, potassium metaphosphate and sodium metaphosphate with water and at least one strong mineral acid

selected from the group consisting of hydrochloric acid, nitric acid, phosphoric acid and sulfuric acid to provide a reaction mixture in the form of a slurry, (2) advancing said reaction mixture with continual agitation along an elongated mixing zone and, by such agitation, initiating hydrolysis of the metaphosphate with said hydrolysis progressing exothermically as said advance and agitation continue, (3) incorporating in said reaction mixture during its advance along said mixing zone neutralizing ammonia in proportion for substantially complete neutralization of the acid constituents of said reaction mixture, and (4) then further advancing said reaction mixture along said mixing zone with continual agitation as said neutralizing ammonia reacts exothermically with said acid constituents and, by such further advance and agitation, causing the reaction mixture to be converted to a substantially fully reacted fertilizer product in the form of solid granules which are substantially homogeneous as to chemical constituency, the proportion of acid employed being in the range of from 0.1 to 1.5 parts by weight per part by weight of said metaphosphate, and the proportion of water employed being 1-5 times the stoichiometric quantity required for complete hydrolysis of the metaphosphate.

4. The process of claim 3, including the additional step of incorporating in said reaction mixture, at a point along said mixing zone which is adjacent the point of addition of said neutralizing ammonia, a fertilizer salt having a negative heat of solution and selected from the group consisting of potassium chloride, potassium sulfate, ammonium sulfate and ammonium nitrate.

5. The method of claim 3 wherein said reaction mixture is advanced along said mixing zone as a continuously moving bed of substantial depth and said step of incorporating neutralizing ammonia in said reaction mixture is

accomplished by injecting a fluid ammoniating agent into said bed along a line adjacent the bottom of the bed and extending in the direction of travel thereof.

6. The method of claim 3 including the additional step of continuing to advance said granular fertilizer product along said zone, then incorporating in said product an additional quantity of fluid ammoniating agent and a quantity of a strong mineral acid sufficient to completely neutralize said additional quantity of ammoniating agent, and further advancing said product with continual agitation to effect reaction of said additional ammoniating agent and acid on the surfaces of the granules of said product.

7. The method of claim 3 including the additional steps of recovering said product from said mixing zone, classifying the product to desired size, returning fines continuously to said reaction product, and packaging the recovered product without further treatment.

8. The process of claim 1 wherein the metaphosphate employed is calcium metaphosphate and the acid employed is sulfuric acid.

9. The process of claim 3 wherein the metaphosphate employed is calcium metaphosphate and the acid employed is sulfuric acid.

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