

High-Analysis Fertilizers from Phosphoric Acid and Conventional Ammoniating Materials

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A process for producing homogeneous, granular, high-analysis fertilizers by the reaction of phosphoric acid with standard ammoniating materials in a rotary cylindrical ammoniator-granulator was studied extensively in a pilot plant. In some tests potassium chloride was fed to the ammoniator and incorporated in the product. Typical products were 11-22-22, 17-17-17, and 30-10-0 ammonium phosphate nitrates, 15-30-15 ammonium phosphate urea, and 7-28-28 ammonium phosphate. Exploratory pilot-plant or laboratory studies also were made of other methods of producing ammonium phosphate nitrate: crystallization; ammoniation in an open tank followed by granulation in a pugmill, prilling, or flaking; and ammoniation in a packed tower to produce an essentially anhydrous melt that could be granulated by prilling or flaking.

AMMONIUM PHOSPHATE FERTILIZERS are being produced in increasing quantities in the United States. These fertilizers have a high plant food content and are highly water soluble. Monoammonium phosphate, diammonium phosphate, and mixtures of these can be produced from electric-furnace or wet-process phosphoric acid. Typical grades being produced in large quantities are 21-53-0, 18-46-0, and 11-48-0.

When ammonium phosphates are used as the base material for granulated mixed fertilizers of higher nitrogen-phosphorus weight ratios, the additional nitrogen is usually incorporated by ammoniation of sulfuric acid, which is included in the formulation. However, costs generally would be lower and products would be of higher analyses if the additional nitrogen were supplied as ammonium nitrate or urea. The Tennessee Valley Authority has made exploratory laboratory and pilot-plant studies of several methods of producing these types of high-analysis fertilizers, called ammonium phosphate nitrate and ammonium phosphate urea. These products were homogeneous mixtures containing ammonium nitrate and ammonium phosphate or urea. The ammonium phosphate generally was present as a mixture of monodiammonium phosphates. Potassium chloride usually was added to give a fertilizer containing the three major plant nutrients. Included were processes involving crystallization; neutralization (ammoniation) of acid in an open tank followed by granulation in a pugmill, prilling, or flaking; and neutralization and evaporation in a packed tower followed by prilling or flaking; as well as ammoniation and granulation in a TVA-type ammoniator-granulator.

Crystallization

Since ammonium nitrate and ammonium phosphate can be produced by crystallization, the feasibility of producing ammonium phosphate nitrate by this method was investigated. The system nitric acid-ammonia-phosphoric acid was studied at 120° F. to determine the effect of pH of mother liquor on the composition of the solid phase. At pH 5.1, the solid phase was a mixture of diammonium phosphate, monoammonium phosphate, and ammonium nitrate crystals. Between pH 5.1 and 6.5, the highest pH studied, the solid phase consisted of diammonium phosphate and ammonium nitrate. In making ammonium phosphate nitrate, it is desirable to ammoniate the phosphate to the diammonium form (9.6 pounds of NH_3 per unit of P_2O_5) rather than to the monoammonium form (4.8 pounds of NH_3 per unit of P_2O_5), since the additional relatively inexpensive ammonia tied up with the phosphate results in an important cost advantage. In producing the diammonium form by crystallization, ammonia loss can be minimized by maintaining the temperature and the pH of the mother liquor sufficiently low to avoid high vapor pressure of ammonia over the solution.

Saturated solutions in equilibrium with ammonium nitrate and diammonium phosphate contain a high concentration of nitrogen but relatively little phosphate. Preliminary data indicated that the liquid phase in equilibrium with ammonium nitrate and diammonium phosphate at 120° F. had an N-to- P_2O_5 weight ratio of about 17—considerably higher than in most fertilizers. At steady-state conditions, nitrogen and phosphate will crystallize in the same ratio in which they are fed; however,

with the N-to- P_2O_5 ratio in the mother liquor so different from that desired in the product, control of product composition would be difficult. A product with a relatively high N-to- P_2O_5 ratio would tend to reduce the variation in grade; therefore, a N-to- P_2O_5 feed weight ratio of 5 was selected. This was calculated to give a mixture of ammonium nitrate and diammonium phosphate containing 33.2% total N and 6.7% P_2O_5 .

The pilot-plant tests were carried out with electric-furnace phosphoric acid. Wet-process acid could be used but the impurities would have to be removed because they would interfere with crystallization. Houston, Yates, and Haunschild have described a method for removing these impurities by precipitating with ammonia and filtering (9).

A flow sheet illustrating the crystallization process is shown in Figure 1. The vacuum crystallizer (9) was a cylindrical, cone-bottomed vessel 18 inches in diameter by 6 feet high. Vapors were withdrawn from the top to a barometric condenser. Vacuum was maintained with a steam ejector. A mixture of electric-furnace phosphoric acid (77% H_3PO_4) and nitric acid (51% HNO_3) was fed to the crystallizer at a constant rate along with ammonia to maintain a pH of 6.5 in the mother liquor. Water was added to maintain a constant level in the crystallizer. The temperature was maintained at about 120° F. by controlling the pressure in the crystallizer at about 2 inches of Hg absolute.

A slurry of crystals was withdrawn through a vacuum tank at 20-minute intervals and centrifuged. The amount removed was regulated to keep the suspension density at about 25 to 35% by volume. The mother liquor from the centrifuge was recycled to the crystal-

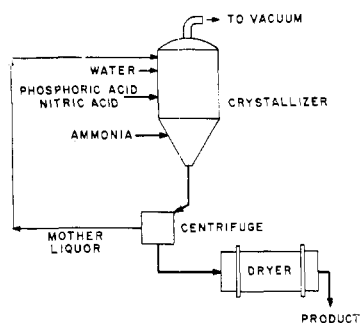


Figure 1. Crystallization process for making ammonium phosphate nitrate

Table I. Production of Ammonium Phosphate Nitrate by Crystallization

Production rate, lb./hr.	30
Crystallizer temperature, ° F.	119
Crystallizer vacuum, in. Hg absolute	2
Mother liquor, pH	6.5
Mother liquor, wt. %	
Total N	26.6
NH ₃ -N	13.5
P ₂ O ₅	1.4
N:P ₂ O ₅ weight ratio	19
Composition of crystalline product, ^a	

	Range	Av.
Total N	33.6-32.8	33.2
NH ₃ -N	17.9-18.0	18.0
P ₂ O ₅	5.4-8.9	7.2
N:P ₂ O ₅ weight ratio	3.8-6.2	4.6
Lb. free NH ₃ /unit P ₂ O ₅	8.5-9.9	9.4

^a Grab samples taken every 4 hours (unconditioned).

lizer. The crystalline product was dried in a rotary dryer.

Data from the tests are shown in Table I. The production rate was about 30 pounds per hour. The product was a mixture of ammonium nitrate and diammonium phosphate crystals. Control of operating conditions was not adequate to obtain a product with a reasonably uniform composition. The P₂O₅ content varied from 5.4 to 8.9%; variation in nitrogen was relatively small (33.6 to 32.8%). Poor control was due, in part, to the nonuniform addition of water to the crystallizer as a result of using steam to clean out the lines through which crystals were withdrawn and mother liquor was returned. When too much water was added, crystals were dissolved, and the N-to-P₂O₅ ratio in the solid phase decreased. When too little water was added, crystallization occurred too rapidly, and the N-to-P₂O₅ ratio in the solid phase increased. Better control of product composition would have been obtained by modifying the equipment to make the rates of crystal removal and water addition more uniform. The crystals were small (-20 mesh), and an agglomeration step would

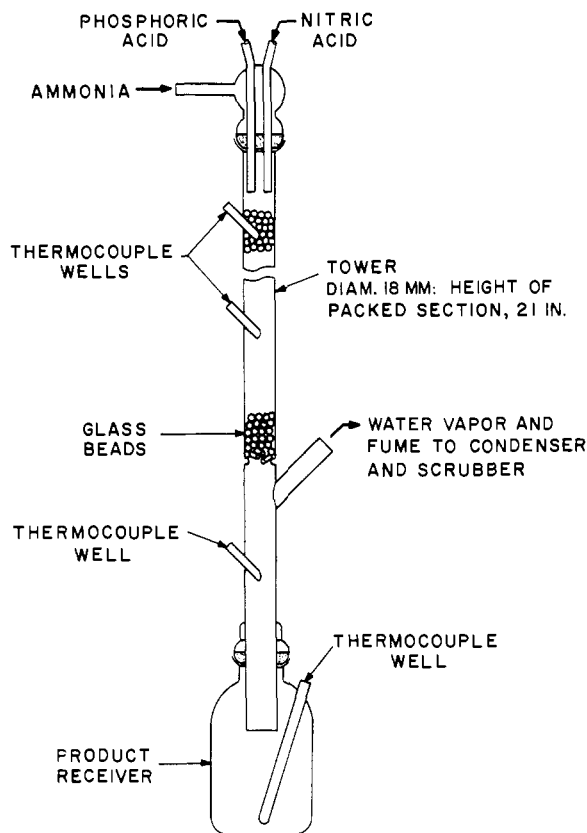


Figure 2. Packed tower reactor for production of ammonium phosphate nitrate

probably be required to produce granular-size material. An agglomeration step also could be used to incorporate potassium chloride in the product.

Neutralization and Evaporation in a Packed Tower

In ammonium nitrate production, many efforts have been made toward combining two or more of the steps involved—neutralization, concentration, granule formation, and drying. Several processes combine the first two (4, 12). In another process (6), ammonia and nitric acid are preheated and then reacted in a packed tower to form ammonium nitrate and water vapor. The latter is removed from the melt in a cyclone-type separator with the aid of hot air. The molten product (about 400° F.) flows onto a water-cooled steel belt where it solidifies, and the resulting flakes are ground to the desired size. The melt contains only about 0.2% water.

Small-scale tests were made of the production of ammonium phosphate nitrates by the packed tower process (Table II). It was recognized that the degree of ammoniation of the phosphoric acid probably would be limited to that for monoammonium phosphate (4.8 pounds of NH₃ per unit of P₂O₅) because of the high temperature in the tower.

The packed tower reactor (Figure 2)

was made of glass and packed with 0.5-cm. glass beads. Nitric acid (60%) and phosphoric acid (60%, electric-furnace type) were preheated and fed into the top of the tower along with ammonia. Because of the difficulty in controlling flow precisely, ammonia was fed in excess in most runs to avoid an acidic condition which might be hazardous. The tower was insulated with 1 inch of magnesia. Because of the high ratio of exterior tower surface to interior volume, heat loss was excessive. Heat to offset this loss was added through a resistance winding on the tower. The molten product from the tower was collected in a receiver, while the gases were passed through a condenser and an acid scrubber to remove ammonium nitrate fume.

The production rate was about 5 to 10 grams per minute. The proportions of nitric and phosphoric acids were varied to obtain products having N-to-P₂O₅ weight ratios of 0.33 to 1 to 2.8 to 1. These products flowed satisfactorily from the tower at about 380° F. When the N-to-P₂O₅ ratio was below 0.33 to 1, the tower plugged even above 400° F. The compositions of the products ranged from 17% N and 50.8% P₂O₅ to 31% N and 10.9% P₂O₅. The moisture content was about 0.1%. About 5 pounds of ammonia were fixed per unit of P₂O₅.

There was considerable loss of ammonium nitrate as fume. This was to be

Table II. Production of Ammonium Phosphate Nitrate in a Packed Tower

Nominal production rate, g./min.	7 ^a	6 ^a	4 ^a	7 ^b	8 ^b	9 ^b
Feed rates, g./min.						
Nitric acid, 60% HNO ₃	2	4	4	7	8	9
Electric-furnace phosphoric acid, 60% H ₃ PO ₄	8	6	3	3	3	3
Ammonia, gaseous anhydrous	1	2	1	2	2	2
Temp., ° F.						
Nitric acid	108	147	147	147	147	147
Phosphoric acid	136	190	190	217	145	145
Tower	378	380	380	383	383	383
Product composition, %						
Total N	17.0	21.3	24.4	29.0	30.3	31.0
NH ₃ -N	13.7	14.8	15.4	16.4	16.4	16.5
Total P ₂ O ₅	50.8	39.2	29.5	16.5	12.8	10.9
Moisture	0.1	0.1	<0.1	0.1	0.1	0.1
N:P ₂ O ₅ weight ratio	0.33	0.54	0.83	1.76	2.37	2.84
Lb. free NH ₃ /unit P ₂ O ₅	5.0	5.1	5.3	5.6	4.7	4.4

^a By weighing samples collected for 30 minutes.^b By calculation from feed rates.^c Unconditioned.**Table III. Pugmill Granulation of Ammonium Phosphate Nitrate**

Nominal production rate, lb./min.	4	4
Reaction tank		
Nitrogen solution feed rate, lb./min.	2(Z) ^a	2(Z) ^a
Phosphoric acid feed rate, lb./min.	1.5(WP) ^b	1.5(EF) ^c
Phosphate rock feed rate, lb./min.	0	0.2
Temperature of material, ° F.	250	247
H ₂ O content of material, %	10	10
Pugmill		
Recycle ratio, lb. recycle/lb. product	4	4
Potassium chloride feed rate, lb./min.	1.5	1.2
Temperature of discharge, ° F.	107	123
Granulator		
Temperature of discharge, ° F.	164	180
Moisture content of discharge, %	1	2
Dryer discharge		
Composition, wt. % ^d		
Total N	16.8	16.8
NH ₃ -N	11.2	11.2
Total P ₂ O ₅	20.2	22.8
Available P ₂ O ₅	19.9	22.6
W. S. P ₂ O ₅	18.2	...
K ₂ O	17.6	16.1
H ₂ O	0.4	0.4
Lb. free NH ₃ /unit P ₂ O ₅	6.8	6.0
Screen analysis, wt. %		
Oversize (+6)	18	12
Onsize (-6 + 20)	63	66
Undersize (-20)	19	22

^a See Table V for composition of solution.^b Wet-process acid (56% P₂O₅).^c Electric-furnace acid (58% P₂O₅).^d Unconditioned.

expected, since the packed tower process depends upon a high rate of throughput to facilitate collection of the fume on the packing. However, because of the violence of the reaction, it was undesirable to operate the glass reactor at a sufficiently high rate to accomplish this.

Since the melt appeared to be fluid enough to prill without difficulty, melts of 24-28-0 ammonium phosphate nitrate at 300° to 360° F. were sprayed into the air from a glass nozzle (0.5-mm. opening) at a height of about 40 feet. Acceptable prills were produced. A recent patent also describes a process for producing a fertilizer prill containing ammonium nitrate and monoammonium phosphate (3).

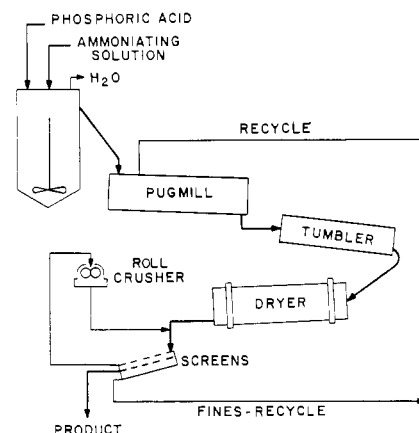
No flaking tests were made since the material appeared to cool and harden in a manner similar to ammonium

nitrate. The solidified cake was brittle and easily broken up.

In a few tests with wet-process phosphoric acid, considerable difficulty was encountered with stoppage in the tower. The impurities in the acid increased the viscosity of the melt and thus impeded flow.

Ammoniation in an Open Tank

In bench-scale and pilot-plant tests, phosphoric acid was ammoniated in an open tank, and the resulting slurry was processed by mixing with recycle fines in a pugmill, or by prilling or flaking. In some tests, ammoniating solution was used. In others, when an ammoniated slurry of lower moisture content was desired, gaseous ammonia and solid ammonium nitrate were used instead of ammoniating solution.

**Figure 3. Pugmill granulation of ammonium phosphate nitrate**

Pugmill Granulation. Granulation in pugmill-type equipment is used in a number of fertilizer processes. In the production of ammonium phosphate sulfate (2) and nitric phosphates (8, 13), slurries resulting from ammoniation of mixed acids or phosphate rock acidulates, respectively, are mixed with product fines in a pugmill, and the damp, solid product is dried and screened. In the production of ammonium nitrate sulfate in Europe (10), a 95% solution of ammonium nitrate is mixed with solid ammonium sulfate and product fines in a double spiral blade mixer. In all these processes, other fertilizer materials, such as potash, can be added in the mixer.

This type of operation was studied in pilot-plant tests in which phosphoric acid was reacted with ammoniating solution in an open tank, and the resulting slurry was granulated with recycle fines in a pugmill. Figure 3 shows the equipment used. The reaction tank had a 12-gallon capacity and was equipped with an agitator. Ammoniating solution and phosphoric acid were introduced through separate spargers near the bottom of the reactor. The ammonia sparger was a drilled pipe; the acid sparger an open pipe. The slurry was discharged through an overflow pipe near the top of the reactor. The pugmill, double shaft, was 6 feet long, 14 inches wide, and 13 inches deep. One shaft had two rows of blades, and the other had three rows; the blades were on 4-inch centers. The shaft with two rows of blades rotated at 47.5 r.p.m., and the other rotated at 31.6 r.p.m. Intermeshing of the blades gave them a self-cleaning action.

The other facilities consisted of a rotary tumbler (10 inches in diameter by 8 feet long; 30 r.p.m.), a rotary dryer, and equipment for screening product, crushing oversize, and recycling fines. A cooler was not used, but this was not a serious handicap because the small quantity of material being handled lost heat to the atmosphere rapidly in the

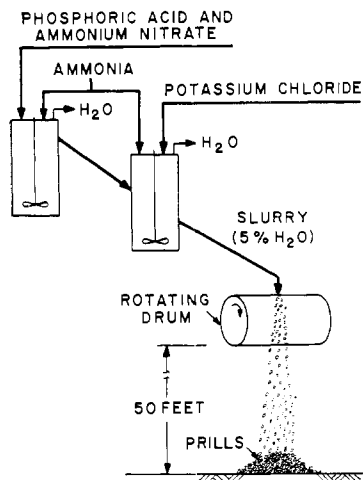


Figure 4. Prilling of ammonium phosphate nitrate

conveying system. A cooler would be required in a large-scale operation.

Data for tests of the production of 16-22-16 granular products are shown in Table III. When electric-furnace acid was used, a small amount of finely ground phosphate rock usually was added to the acid (5 to 10% of the total P_2O_5) to aid granulation.

It was desirable to ammoniate the phosphoric acid to as high a degree as possible without excessive loss of ammonia—6 to 7 pounds of ammonia per unit of P_2O_5 ($NH_3:H_3PO_4$ mole ratio of 1.3 to 1.5). This range is near that which gives maximum solubility in the system monoammonium phosphate-diammonium phosphate-water. Judging from the odor of ammonia over the reaction tank, the loss of ammonia was not excessive.

As a result of the heat of reaction of the acid and ammoniating solution, the temperature of the slurry was 250° F., and about half of the water in the feed materials was evaporated. The ammoniated slurry contained 10 to 12% water and was fluid at the operating temperature.

In tests with wet-process acid, gelling or solidification occurred in the reaction tank when the water content was 10 to 12%, and the degree of ammoniation was allowed to fall below about 5 pounds of ammonia per unit of P_2O_5 .

The slurry was pumped continuously from the reactor to the pugmill and granulated by mixing with product fines. Potassium chloride usually was added to the pugmill to give a three-component fertilizer. The moisture content of the material in the pugmill was decreased to about 1 to 2% to avoid overagglomeration. This required about 4 pounds of recycle fines per pound of dry product. The granules leaving the pugmill were weak. Stronger granules were obtained by passing the material from the pugmill through the rotary

Table IV. Prilling Ammonium Phosphate Nitrate

Production rate, lb./min.	3
First reaction tank ^a	
pH	2.0
Temperature, ° F.	260
H ₂ O, %	5.7
Lb. free NH ₃ /unit P ₂ O ₅	4
Second reaction tank ^a	
pH	5.5
Temperature, ° F.	284
H ₂ O, %	4.0
Lb. free NH ₃ /unit P ₂ O ₅	6.6
Prilled product, cumulative % retained on indicated screen size	
6 mesh	0
8 mesh	2
12 mesh	30
14 mesh	65
16 mesh	82
Chemical composition of prilled product ^b (dry basis), %	
Total N	17.5
NH ₃ -N	11.3
P ₂ O ₅	18.6
K ₂ O	20.0
H ₂ O	3.4
Lb. free NH ₃ /unit P ₂ O ₅	6.6

^a Mixture of electric-furnace acid and crystalline ammonium nitrate reacted with anhydrous gaseous ammonia in two stages.

^b Unconditioned.

tumbler and heating to about 175° F. with a gas flame. If the tumbler were omitted, similar results probably could be obtained by omitting the lifting flights from the feed end of the dryer.

The granules were dried to a moisture content of about 0.5%. The discharge from the dryer was screened to separate product-size material (-6 +20 mesh), which amounted to about 65% of the total. The oversize was crushed and recycled to the pugmill together with the fines; some onsize product also was ground for recycle as needed.

The highest N-to- P_2O_5 weight ratio obtainable with commercially available ammonia-ammonium nitrate solution was about 0.8. Therefore, gaseous ammonia and solid ammonium nitrate were used in tests of the production of 1 to 1 N-to- P_2O_5 weight ratio fertilizers. The ammonium nitrate was premixed with electric-furnace phosphoric acid before it was fed to the reaction tank. With these materials, the moisture content of the ammoniated slurry was only about 6% and the amount of recycle required was 2.5 pounds per pound of product. The retained degree of ammoniation was 6.5 to 7.0 pounds of ammonia per unit of P_2O_5 . Grades produced were 25-25-0 and 17-17-17.

Prilling and Flaking. Ammonium nitrate usually is produced by prilling or flaking. In these processes, molten ammonium nitrate is converted to a solid by cooling. Ordinarily, water is removed by preconcentration and by drying the finished granules. For example, in most ammonium nitrate

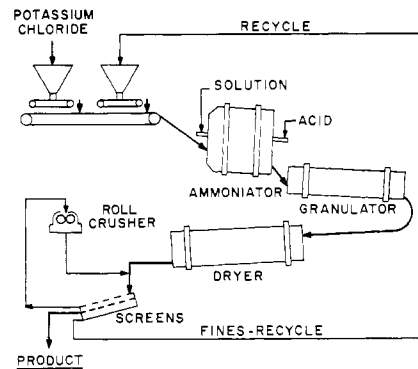


Figure 5. Production of ammonium phosphate nitrate in the TVA continuous ammoniator

prilling plants, ammonium nitrate solution is first concentrated to about 95%. The concentrated solution is sprayed into the top of a prilling tower to form drops, which solidify during fall through the tower and are then dried (12).

A few exploratory studies were made to determine the suitability of a prilling process for producing ammonium phosphate nitrate. Figure 4 shows the process flow sheet.

In initial tests with a single ammoniating stage, the reaction was rather violent, and control of the overflow was difficult. Therefore, in most tests, two or three stages of ammoniation were used. Operating data for the production of an 18-18-18 grade are shown in Table IV. The ammonium phosphate nitrate slurry was produced continuously using gaseous ammonia, crystalline ammonium nitrate, potassium chloride, and electric-furnace phosphoric acid (80% H_3PO_4) as raw materials. The ammonium nitrate and phosphoric acid were premixed and pumped continuously into the first ammoniating tank (8 inches in diameter by 12 inches effective height). The partially ammoniated solution overflowed into a second ammoniating tank of the same size, where potassium chloride was added. The retention time in each tank was about 16 minutes. The solution was ammoniated to a pH of about 2.0 (4 pounds of NH_3 per unit of P_2O_5) in the first tank and to a pH of 5.5 (6.6 pounds of NH_3 per unit of P_2O_5) in the second. Judging from the ammonia odor over the tanks, the loss of ammonia was high when the pH was increased above 5.5. The temperature was 260° F. in the first tank and 284° F. in the second. The overflow (200 pounds per hour) from the second tank containing about 4% moisture was formed into drops by a spray nozzle, a drum rotating on a horizontal axis, or a rotating horizontal disk.

The use of a spray nozzle was abandoned because it was difficult to keep the orifice open. Clogging was caused by frozen melt and undissolved potassium chloride particles.

Good results were obtained with the drum and the disk. The drum was 9 inches in diameter and 6 inches wide and rotated at about 750 r.p.m. The disk was 4 inches in diameter and rotated at 900 r.p.m. The drops were allowed to fall onto a floor 50 feet below. The drops from the drum fell in a space 3 to 4 feet in width and 20 feet long; those from the disk were thrown out in a circular pattern about 20 feet in radius. Most of the drops solidified to form well rounded, uniformly sized prills with either the disk or the drum (about 80% - 8 + 16 mesh). The prilled product contained about 3% moisture.

A third ammoniating tank (10 inches in diameter by 14-inch effective height) was added to ascertain whether additional ammonia could be retained in the solution. Operation of the bench-scale equipment was unchanged, except that the overflow from the second ammoniator was fed to the third ammoniator and then to the drum. It was possible to operate the third tank at a pH of about 5.8 (7.2 pounds of NH₃ per unit of P₂O₅) without excessive loss of ammonia. The overflow from the third tank (280° F.) contained 2.5% moisture; the prilled product contained 1.4% moisture and was an 18-18-18 grade. The prills had about the same screen size as those made in the earlier tests. Since they tended to cake, drying or conditioning would be required unless the moisture content of the ammoniated solution was reduced before or during prilling.

In one process for flaking ammonium nitrate, a hot concentrated solution of ammonium nitrate flows onto one end of a continuous stainless steel water-cooled belt, and the solidified material is discharged as a thin sheet from the other end (6). The sheet is broken up,

crushed, and screened. In laboratory tests of flaking ammonium phosphate nitrate, the reaction tanks were the same as for the prilling tests. The slurry from the second tank, containing about 5% water, was collected in thin sheets in water-cooled pans. The feed rate was about 3 pounds per minute. The material solidified at about 200° to 225° F. and was easily removed from the pan. The sheets were broken into granular-size material with a knife-type hammer mill. The granules (18-18-18 grade) were dried and screened. The fines were returned to the reaction tank.

Both electric-furnace and wet-process acids were used in the prilling and flaking tests. With wet-process acid, intermediate pH's were avoided, since gelling usually occurred in the reaction tank in the approximate pH range of 2 to 5. The exact pH range in which gelling occurred was not determined.

Some grades of ammonium phosphate nitrate could be produced by prilling or flaking. Although the point was not clearly determined, it is believed that the slurry feed to the prilling operation should not contain over 4 to 5% H₂O. This probably could be produced by reacting phosphoric acid and ammoniating solution and evaporating excess water; it would be desirable to neutralize in stages and carry out most of the evaporation at a relatively low degree of ammoniation to avoid excessive loss of ammonia. The evaporation probably would not be required if an essentially anhydrous ammoniating solution (about 0.5% H₂O) were used. This type of solution was not available commercially at the time of these tests. Using ammoniating solution rather than ammonia and ammonium nitrate usually would be more economical.

Simultaneous Ammoniation and Granulation

Simultaneous ammoniation and granulation in a TVA-type continuous ammoniator were tested because this type of equipment could be used with many formulations, and many fertilizer plants have such equipment in operation. The results of exploratory tests were very promising, and extensive studies were made on a pilot-plant scale.

Pilot Plant and Procedure. A flow sheet of ammonium phosphate nitrate production in the TVA continuous ammoniator pilot plant (5) is shown in Figure 5. The facilities consisted of a rotary drum ammoniator, a granulator, a dryer, and equipment for feeding and metering liquids and solids, screening product, crushing oversize, and recycling fines. The ammoniator, granulator, and dryer were made of mild steel.

The raw materials (Table V) in nearly all the pilot-plant tests were typical of those available to commercial fertilizer producers. The ammoniator, 3 feet in diameter and 3 feet long, did not contain flights. It was operated at a slope of 1 inch per foot and a speed of 15 r.p.m. It had a scraper bar of 2-inch angle iron for continuous cleaning of the inside wall and retaining rings for maintaining a 9-inch bed of solids.

Ammoniating solution or ammonia was fed through a distributor 30 inches long and positioned 5 inches below the surface of the rolling bed of solids in the ammoniator. The distributor used in most of the tests was of the slotted type (14); equally satisfactory results were obtained with a distributor made from 1/2-inch stainless steel pipe with 19 equally spaced holes. The phosphoric acid was fed through a 23-inch-long

Table V. Typical Analyses of Raw Materials

Raw Material	Chemical Analysis, %									Screen Analysis (Tyler), %				
	N	Total	P ₂ O ₅ C.I.	W.S.	K ₂ O	SO ₃	Fe ₂ O ₃	Al ₂ O ₃	H ₂ O	+6	+28	+48	+100	-100
Phosphoric acid														
Electric furnace	...	56.5
Wet process	...	54.6	2.9	1.2	0.9
Concentrated superphosphate	...	50.6	0.9	45.9	0.6	0	1.2	7.2	50.9	40.7
Phosphate rock	...	31.8	1.0	0	0	0	9.9	90.1
Potassium chloride														
Medium size	60.8	0.3	0	20.2	44.0	29.9	5.9
Fine size	60.7	0.2	0	0.8	6.5	71.8	21.0
Ammonium nitrate crystals														
Undried, unconditioned	34.7	1.0	0	52.9	35.1	11.0	1.0
Dried, conditioned	33.6	0.1	0	50.7	42.8	5.6	0.9
Diammonium phosphate	20.8	53.7	0.0	53.7	0.06	0	55.4	29.4	12.9	2.3
Ammonium sulfate	21.1	0.3	0	13.5	59.9	20.7	6.0
Iron ore	70.2	0	0	0.8	9.5	89.7
Composition of Ammoniating Solution, %														
Type	Free ammonia	Ammonium nitrate	Urea	Ammonium carbamate	H ₂ O	Total N								
X	22.2	65.0	12.8	41.0								
X-6	25.0	69.0	6.0	44.8								
Z	16.6	66.8	16.6	37.0								
Z-7	19.0	74.0	7.0	41.4								
U-C	24.1	0	43.3	15.0	17.6	45.5								

distributor made from 1/4-inch stainless steel pipe with 24 holes spaced 1 inch apart. The flow of acid started 2 to 3 inches nearer the feed end of the ammoniator than the flow of ammonia, to prevent ammonia from coming in contact with that portion of the bed that did not contain acid. Equally satisfactory results were obtained with the acid fed on top or below the surface of the bed. When the acid distributor was under the bed, it was positioned adjacent to the leading edge of the ammonia distributor and the holes were faced upward.

In a few tests, a small amount of sulfuric acid was used in the formulation; for convenience, the sulfuric acid and phosphoric acid were premixed and distributed under the bed. The acid mixture is corrosive to stainless steel and, for prolonged operation, it should be fed in separate streams to a mixing tee just before the distributor. The mixing tee and distributor could be built from corrosion-resistant material such as Hastelloy C.

To obtain satisfactory granulation, it was necessary to use sufficient recycle to reduce the moisture content of the feed to the ammoniator (including recycle) to 4 to 6% in most tests. The recycle to the ammoniator usually was in the range of 90° to 120° F. In most tests, jets of air (5,000 to 11,000 cubic feet per ton of product) were directed onto the bed to help control the size of the granules; the air was introduced through a perforated pipe parallel to the axis of the ammoniator and about 4 inches above the surface of the bed of solids.

The granular material was discharged from the ammoniator at 150° to 200° F. and passed through the 2- by 6 1/2-foot long granulator. The product from the granulator, which usually contained 2 to 3.5% moisture, was fed to the dryer, which was 3 feet in diameter by 24 feet long. Heat was supplied concurrently by the combustion of natural gas in an adjacent chamber. The temperature of the material discharged from the dryer usually was below 200° F. to avoid decomposing the diammonium phosphate in the product. Although some improvement in roundness and hardness of the granules occurred in the granulator, it is believed that this piece of equipment could be omitted without harmful effect, particularly if there were no lifting flights in the feed end of the dryer.

A cooler was not used in the pilot plant because the relatively small quantity of material lost heat rapidly in the conveying system. In a commercial plant, a cooler would be required. For most grades, it would be preferable to cool all the throughput, since the use of cooled recycle would decrease the temperature in the ammoniator and the amount of recycle required. How-

ever, in formulations such as for 30-10-0, which result in relatively little heat of reaction and have a predominance of ammonium nitrate, it would be desirable to cool only the onsize product and return the hot recycle to the ammoniator.

The material from the dryer usually was screened to separate +6-mesh material as oversize and -16 mesh as undersize. A double-roll crusher was used for crushing the oversize. When the temperature of the material fed to the crusher was over 140° F., some "pancaking" occurred during crushing; no difficulty was encountered with properly cooled material. The undersize and crushed oversize were recycled to the ammoniator.

Production rates of 0.5 to 1.0 ton per hour were used in most tests. The capacities of the dryer and recycle system were exceeded at rates higher than 1 ton per hour.

Operating Results

Additives Used to Promote Granulation. An arbitrary criterion for good granulation in the pilot plant was that 50% or more of the product from the granulator should be -6 +16 mesh. In some tests with electric-furnace acid, the material in the granulator was not sufficiently plastic to granulate properly. The difficulty was overcome by adding small quantities of phosphate rock, concentrated superphosphate, or iron ore as follows:

Finely ground phosphate rock to supply 5 to 10% of the P₂O₅ in the product was mixed with the phosphoric acid in a cone-type funnel mixer (15), and the resulting slurry was distributed over the rolling bed of material in the ammoniator. The distributor (7) was an open-end pipe that was moved back and forth over the length of the bed at about 28 passes per minute.

Concentrated superphosphate to supply about 15% of the P₂O₅ in the product was ground to -48 mesh and added with the other dry materials fed to the ammoniator.

Finely ground iron ore was added to the phosphoric acid at the rate of 10 to 20 pounds per ton of product. The ore and acid were fed continuously to a small mixing tank, from which the mixture was pumped to the ammoniator through the acid distributor.

Good granulation efficiency was obtained in most of the tests, and 60 to 70% of the product from the granulator was of the desired size. There was little change in particle size during drying. When the amount of undersize and oversize was less than that required for recycle, additional material for recycle was obtained by crushing some of the onsize product.

Degree of Ammoniation and N-to-P₂O₅ Ratio. When phosphoric acid was reacted in the continuous ammoniator with ammoniating solution or am-

monia, about 7 pounds of ammonia per unit of P₂O₅ could be fixed without excessive loss of ammonia. At this degree of ammoniation, about half of the P₂O₅ is present as diammonium phosphate and half as monoammonium phosphate. In most tests, less than 3 pounds of ammonia per ton of product were lost. When calculating formulations in which part of the P₂O₅ was supplied as concentrated superphosphate, it was assumed that the superphosphate would fix 3.8 pounds of ammonia per unit of available P₂O₅. This degree of ammoniation of concentrated superphosphate generally is used in other types of formulations (5).

The N-to-P₂O₅ ratio in the product depended on the degree of ammoniation of the phosphoric acid and the ratio of free to fixed nitrogen in the solution. The N-to-P₂O₅ ratio could be increased by adding sulfuric acid to fix additional ammonia or by adding supplemental nitrogen such as solid ammonium nitrate or ammonium sulfate.

In Table VI the formulations represent actual weights of materials used and are slightly different from the calculated formulation because of inaccuracies in feeding.

N-to-P₂O₅ Weight Ratios of 0.8 and 1.0. The highest N-to-P₂O₅ weight ratio that could be obtained when commercially available ammonia-ammonium nitrate solution and phosphoric acid were used was slightly less than 0.8. Ammonium phosphate nitrate products of about this ratio were obtained when solution Z or Z-7, with a free to fixed nitrogen weight ratio of about 0.6, was used. About 7 pounds of ammonia per unit of P₂O₅ were fixed. At the time of the tests, solutions having a lower proportion of free ammonia were not available commercially.

A 16-22-16 grade was made using solution Z (test H-21). A 17-17-17 grade was made in tests H-32 and H-54 by using solution Z or Z-7 and adding sulfuric acid to fix additional nitrogen, or by supplying 7 pounds of ammonia as liquid ammonia per unit of P₂O₅ and the rest of the nitrogen as solid ammonium nitrate (test H-4). A 15-15-15 grade was made by supplying 3.6 units of P₂O₅ as concentrated superphosphate, 11.4 units as phosphoric acid, 5.2 units of nitrogen as ammonium sulfate, and 9.8 units as solution Z-7 (test H-55). Electric-furnace phosphoric acid was used in these tests.

The amount of recycle required depended on the proportion of water and ammonium nitrate in the charge to the ammoniator, as shown by the data at top of page 357.

The 16-22-16 and 17-17-17 formulations contained 32 to 35% ammonium nitrate. When all of the nitrogen was supplied as solution Z (16.6% H₂O), the charge contained 13 to 14% water,

Total N	17.1	16.9	17.5	16.7	16.2	12.4	7.9	8.6	5.7	15.4	8.0	15.2	31.4	28.3	15.5
NH ₃ -H	11.6	10.8	11.7	11.2	12.7	8.6	5.1	6.5	5.1	13.4	7.3	15.2	17.7	16.2	9.0
Total P ₂ O ₅	21.7	18.6	16.3	16.6	15.9	23.1	16.2	18.1	18.8	46.9	26.7	52.6	11.2	14.7	30.5
Available P ₂ O ₅	21.6	18.3	16.2	16.6	15.8	22.3	16.2	18.0	18.8	46.8	26.6	52.3	11.2	14.7	30.4
W.S. P ₂ O ₅	21.4	17.0	16.1	16.1	14.5	21.1	15.6	16.9	17.9	44.0	25.1	48.9	11.0	13.6	29.0
K ₂ O	17.7	17.8	18.7	19.2	16.5	22.2	35.1	32.5	37.9	2.8	28.3	0.0	0.0	0.0	15.1
H ₂ O	0.8	0.6	0.6	0.1	0.2	0.7	0.4	0.6	1.3	0.7	0.9	1.1	0.5	0.4	0.8
SO ₄	5.5	16.5	3.6

^a EF, electric furnace (see Table V); WP, wet process (see Table V).

^b Identification given in parenthesis (see Table V).

^c L, liquid; G, gaseous.

^d Per cent nitrogen given in parenthesis (see Table V).

^e M, medium size (see Table V); F, fine size (see Table V).

^f Includes water or steam added to ammoniator or granulator.

^g -6 +12.

^h -6 + 20.

and about 6000 pounds of recycle per ton of product were required. When solution Z-7 (7% H₂O) was used in the 17-17-17 formulation, the water in the charge was decreased to 9%, and the amount of recycle required was decreased to 4600 pounds. When solid ammonium nitrate and liquid ammonia were used instead of nitrogen solution, the water in the charge was 6% and 2800 pounds of recycle were required. In the 15-15-15 formulation, the charge also contained 6% water; however, only about 1800 pounds of recycle were required because considerably less ammonium nitrate was present.

Phosphate rock was added as a granulation aid in the formulation for the 17-17-17 fertilizer made with solid ammonium nitrate and liquid ammonia (test H-4); however, this test was made in the early part of the work, and it is believed that satisfactory granulation could be obtained without the granulation aid.

N-to-P₂O₅ Weight Ratio of 0.5. Ammonium phosphate nitrate fertilizers with N-to-P₂O₅ weight ratio of 0.5 were made when all of the nitrogen was supplied as a nitrogen solution having a free nitrogen to fixed nitrogen weight ratio of about 0.8. An 11-22-22 grade was made using solution X and electric-furnace phosphoric acid (test H-11). An 8-16-32 grade was made using solution X or X-6 and wet-process phosphoric acid (tests H-50 and H-59). Fine-size potassium chloride was used in test H-59, and medium-size potassium chloride was used in the other tests.

These grades contained 13 to 21% ammonium nitrate. The amount of recycle increased from about 1500 pounds per ton of product when the charge contained 8% water (8-16-32, tests H-50 and H-59) to 2000 pounds when the charge contained 10% water (11-22-22, test H-11).

To render the material more plastic in the ammoniator when making the 11-22-22 grade with electric-furnace acid, about 2 units of P₂O₅ were supplied as finely ground phosphate rock pre-mixed with the acid.

In tests of the 8-16-32 grade, a granulation aid was not required with medium-size potassium chloride (test H-50),

but was required with fine-size potassium chloride (test H-59). The use of 20 pounds of iron ore per ton of product resulted in excellent granulation.

An ammonium phosphate urea product of 15-30-15 grade was made using an ammonia-urea-ammonium carbamate solution as the ammoniating medium (test H-34). The other raw materials were electric-furnace phosphoric acid, potassium chloride, ammonium sulfate, and concentrated superphosphate (4.4 units of P₂O₅), which was added to aid granulation. About 1.1 units of nitrogen were added as ammonium sulfate, since supplemental nitrogen was required to make grade. Only about 1800 pounds of recycle per ton of product were required to control granulation, even though the amount of water in the charge to the ammoniator was relatively high (13% H₂O). The low recycle rate was attributed to the absence of ammonium nitrate in the formulation and to the presence of ammonium carbamate in the solution, which had an endothermic heat of reaction when it decomposed to ammonia and carbon dioxide.

N-to-P₂O₅ Weight Ratios <0.5. Ammonium phosphate fertilizers of 0.25 and 0.30 N-to-P₂O₅ weight ratios (7-28-28 and 15-50-0 grades) were made by supplying all the nitrogen as anhydrous ammonia. For fertilizers of ratios between 0.30 and 0.50 (for example, 6-18-36 and 16-48-0; ratio, 0.33), a combination of anhydrous ammonia and nitrogen solution was used.

In these tests, the anhydrous ammonia was supplied as liquid rather than gaseous ammonia in order to utilize the cooling effect of vaporization of the liquid ammonia. It usually was necessary to add some water with the liquid ammonia to prevent freezing around the distributor and formation of frozen lumps, which interfered with granulation. Usually, about 0.5 to 1 pound of water per pound of ammonia was adequate. The liquid ammonia and water were mixed in a pipe tee just before entering the distributor. When nitrogen solution also was used, it was mixed with the liquid ammonia and water.

Good granulation was obtained in tests of production of 6-18-36 and

Test No.	Grade	Source of Nitrogen	Charge to Ammoniator, Wt. %		Recycle Required, Lb./Ton of Product
			Water	Ammonium nitrate ^a	
H-21	16-22-16	Solution Z	14	33	5760
H-32	17-17-17	Solution Z	13	33	5880
H-54	17-17-17	Solution Z-7	9	32	4560
H-4	17-17-17	Anhydrous ammonia and solid ammonium nitrate	6	35	2760
H-55	15-15-15	Solution Z-7 and ammonium sulfate	6	19	1830

^a Dry basis.

Table VII. Calculated Formulations for Ammonium Phosphate and Ammonium Phosphate Nitrate

Material	Grade	Pounds per Ton of Product										
		17-17-17	15-15-15	11-22-22	16-48-0	30-10-0	28-14-0	8-16-32	6-18-36	7-28-28	12-24-12	15-50-0
Phosphoric acid, wet process	75% H ₃ PO ₄	625	425	809	1767	368	516	589	663	1031	883	1,840
Ammoniating solution ^a												
Z-7	...	826	481
X	547	194	75	...	596	...
X-6	362
Anhydrous ammonia	301	71	100	...	111	173	...	370
Ammonium nitrate	35% N	1550	1370
Ammonium sulfate	20.5% N	...	500
Potassium chloride	60% K ₂ O	548 ^b	500	733	1067	1200	933	400	...
Concentrated superphosphate	46% P ₂ O ₅	...	150
Sulfuric acid	93% H ₂ SO ₄	104
Iron ore	10	10	20
Conditioner	...	57	42	80	69	66	89	72	63	31	80	60
Filler	32	262	85
Recycle	...	4500	2000	2500	7000	1500	1500	1500	2000	2000	3000	16,000

^a See Table V for solution composition.

^b 62% K₂O.

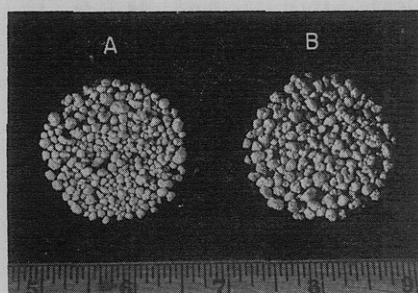


Figure 6. Photograph of 8-16-32 ammonium phosphate nitrates

- A. Made with fine-size potassium chloride
- B. Made with medium-size potassium chloride

15-50-0 grades (tests H-53 and H-76) with wet-process phosphoric acid. Electric-furnace phosphoric acid was used in making 16-48-0 and 7-28-28 grades (tests H-30 and H-23); about 15% of the total P₂O₅ was added as concentrated superphosphate to aid granulation. The 7-28-28 grade was exceptionally difficult to granulate and, for satisfactory results, about 80 pounds of water per ton of product were added to the granulator. In these formulations, which contained relatively little or no ammonium nitrate, the quantity of recycle required increased as the amount of water in the feed to the ammoniator-granulator was increased (see data below).

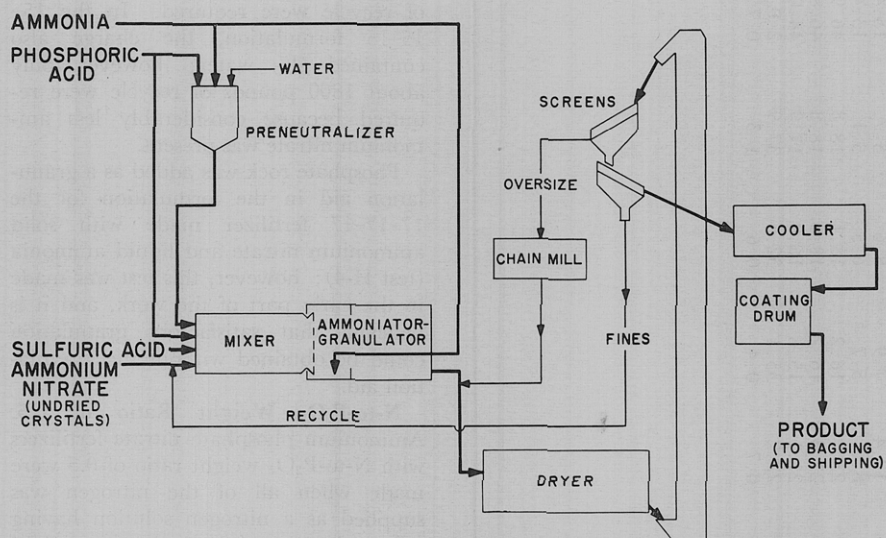


Figure 7. TVA plant for production of 30-10-0 ammonium phosphate nitrate

In later tests by TVA, granular diammonium phosphate was made by a process involving partial preneutralization of phosphoric acid in a tank, followed by completion of the reaction to diammonium phosphate in the ammoniator-granulator drum. It was necessary to feed an excess of ammonia to the drum and recover the excess (1). A recent patent (11) also describes a

process for making diammonium phosphate in a rotary drum ammoniator.

N-to-P₂O₅ Weight Ratios >1. To make grades with N-to-P₂O₅ weight ratios greater than 1, gaseous ammonia was used to neutralize the phosphoric acid and supplemental nitrogen was added as solid ammonium nitrate (tests H-49 and H-44). Gaseous ammonia was used because the amount of acid was small and the maximum amount of heat was desired from the neutralization.

The formulations contained 70 to 80% ammonium nitrate. In the initial tests, control of granulation was difficult, and most of the material discharged from the ammoniator was oversize or undersize, even when granulation aids were used. Bed rolling action was improved by shortening the length of the ammoniating section from 36 to 23 inches.

A 28-14-0 grade was made with

Test No.	Grade	Charge to Ammoniator, Wt. %		Recycle Required, Lb./Ton of Product
		Water ^a	Ammonium nitrate ^b	
H-53	6-18-36	10	3	1,920
H-23	7-28-28	12	0	1,980
H-30	16-48-0	17	11	6,930
H-76	15-50-0	29	0	16,000

^a Includes water added to ammoniator or granulator.

^b Dry basis.

gaseous ammonia, wet-process phosphoric acid, and conditioned crystalline ammonium nitrate. About 2.5 units of the P_2O_5 were supplied as concentrated superphosphate to promote granulation, and 4.2 units as diammonium phosphate. About 68 pounds of steam per ton of product were introduced into the ammoniator to aid granulation.

In making a 30-10-0 grade, the raw materials were undried, unconditioned crystalline ammonium nitrate, electric-furnace phosphoric acid, and gaseous ammonia. About 10 pounds of iron ore per ton of product were premixed in a ribbon mixer with the phosphoric acid to promote granulation. Granulation of this grade was not good when the phosphoric acid was added in the ammoniator. Satisfactory granulation was obtained by premixing about one half of the acid with the solid ammonium nitrate and recycle fines, feeding the mixture to the ammoniator, and adding the remainder of the acid in the ammoniator. Steam was added to the ammoniator to aid granulation.

The moisture in the feed, including recycle, was about 6%, and 1200 to 1500 pounds of recycle per ton of product were required to control granulation. However, about 2000 pounds of recycle were used in the 30-10-0 product to prevent an accumulation of fines.

Calculated Formulations

Calculated formulations for some of the products made in the pilot plant (Table VII) were based on the assumption that wet-process phosphoric acid containing 75% H_3PO_4 and 5% impurities would be used. In some cases, the formulation was changed from that used in the pilot plant in order to use more readily available raw materials or to take advantage of improved technology resulting from later experience in the pilot plant.

Chemical and Physical Properties

The citrate solubility of the P_2O_5 in the products was 99 to 100% except when phosphate rock was used in the formulation. When 10% of the P_2O_5 was supplied as phosphate rock, about 97% of the P_2O_5 in the product was citrate soluble. The water solubility of the P_2O_5 in the product was 91% or higher in all tests.

There was considerable variation in the shape and degree of roundness of the various products (see Figure 6). In the high potash grades (8-16-32 and 6-18-36), fairly well rounded granules were obtained when fine-size potash was used. Medium-size potassium chloride resulted in irregular-shaped granules to which individual particles of potassium chloride were cemented.

Bag-storage tests (Table VIII) were carried out in an unheated building

Table VIII. Results of Bag-Storage Tests

Grade	Moisture Content before Conditioning or Curing, %	Ammonium Nitrate in Product, %	Condition after 3 Months ^a										
			Unconditioned Product			Conditioned Product							
			Not Cured	Cured ^b	Conditioner	Not Cured	Cured ^b	Conditioner					
15-30-15	0.9	0	Hard	Hard	3	2.5% kaolin	Medium	Medium	0	Medium	0		
7-28-28	0.3	0	...	Medium	0	2% kieselsguhr	...	Light	Light	0	Light	0	
16-48-0	0.4	11	Hard	Hard	0	2% kaolin	Hard	Hard	0	Hard	0	Hard	0
16-48-0	1.4	11	Hard	Hard	0	2.5% kaolin	Hard	Hard	0	Hard	0	Hard	0
6-18-36	1.1	3	Hard	Hard	2	3% kaolin	Hard	Light	0	Light	0	Light	0
8-16-32	0.4	13	Hard	Hard	0	4% kaolin	Hard	Hard	4	Hard	0	Light	0
16-22-16	1.0	33	Hard	Hard	6	2% kaolin	Hard	Hard	0	Hard	0	Light	0
16-22-16	0.8	33	Hard	Hard	18	2% kieselsguhr	Hard	Hard	0	Hard	0	Light	0
17-17-17	0.8	33	Hard	Hard	11	5% kaolin	Hard	Hard	0	Hard	0	Light	0
30-10-0	0.4	78	4% kaolin	Hard	Hard	0	Hard	0	Medium	0
			2.5% kaolin	Hard	Hard	8	Hard	0	Medium	0
			3% kaolin	Light	Light	0	Light	0
			3% kieselsguhr	0	...	0
			3% calcined fuller's earth ^e	0	...	0
30-10-0	0.3	78	3% kaolin	Medium	Medium	0	Medium	0
			3% kieselsguhr	Medium	Medium	0	Medium	0
			3% calcined fuller's earth ^e	Light	Light	0	Light	0

^a Bags in eighth to twelfth position from top, except 30-10-0 which was in eighth position in lower of two ten-bag-high pallets.

^b Cured in pile for 7 days.

^c Per cent +2-mesh lumps remaining after four drops.

^d Excessive lumps in 1 month.

^e Average particle size of 8 microns.

under conditions simulating warehouse storage. Six-ply paper bags (80-lb. capacity) having two asphalt-laminated plies were used. Except for the 30-10-0 ammonium phosphate nitrate, all the products were stored in stacks 12 bags high; the bags in the eighth to twelfth positions from the top were examined for bag set and caking. The 30-10-0 product was produced in large-scale equipment and stored two pallets high, 10 bags high per pallet; the eighth bag on the lower pallet was examined. Bag set was determined before moving the bag from its storage position. Caking was determined by measuring the proportion of +2-mesh lumps remaining after the bag had been dropped four times from a height of 3 feet, once on each face and side. The tests included studies of the effects of curing and coating the products with conditioning agents. Kaolin clay was tested on all the products. Kieselguhr and a calcined pulverized fuller's earth were tested on some products. The four-drop test was used in evaluating the storage properties of fertilizers at the time this work was being done. However, the demand for superior products now dictates that evaluations be made without dropping the bags or dropping them only once. Recent experience indicates that material found to have light to medium bag set and no lumps after four drops would contain little or no lumps after the bag had been dropped once.

Products containing less than 40% ammonium nitrate and dried to a moisture content of about 1% or less stored satisfactorily when conditioned with 2 to 3% kaolin or kieselguhr; calcined fuller's earth was not tested. It generally was beneficial to pile-cure products that contained potash prior to conditioning

and bagging. Products containing a large amount of ammonium nitrate, such as 30-10-0, stored satisfactorily when dried to 0.4% moisture and conditioned with 3% kieselguhr or pulverized calcined fuller's earth. Kaolin was somewhat less effective in grades having large amounts of ammonium nitrate. Only the 7-28-28 grade stored satisfactorily without conditioner.

In bulk-storage tests of conditioned products, a few tons were held in an open bin in an unheated building for 3 months. During periods of high humidity, the top 1-inch layer of products containing a large amount of ammonium nitrate became damp or wet. However, the material under this layer was dry and free flowing. Under extended conditions of high humidity, the depth of moisture penetration may exceed the 1 inch noted in these tests, and steps should be taken to protect materials from excessive exposure.

Economics

Cost estimates indicated that the continuous ammoniation process should be economical when the phosphoric acid is available at a favorably low price. Table IX compares costs of an ammonium phosphate urea product and an ammonium phosphate nitrate product with conventional granular fertilizers using raw material costs believed to be typical of a midwestern location. The plant operating cost was assumed to be somewhat higher for the production of the ammonium phosphate nitrate and ammonium phosphate urea products than for the production of conventional fertilizers because of the higher recycle rate required.

The delivered, bagged cost per unit of plant food in the 15-30-15 ammonium

phosphate urea is \$0.07 lower than in the 10-20-10 conventional fertilizer, and in the 17-17-17 ammonium phosphate nitrate is \$0.11 lower than in a 12-12-12 conventional product (Table IX). The lower cost of the 15-30-15 and 17-17-17 products is due primarily to their higher plant food content, which results in savings in bagging, handling, and transportation.

Production of 30-10-0 Ammonium Phosphate Nitrate in a Demonstration Plant

After the pilot-plant project was completed, TVA began producing 30-10-0 ammonium phosphate nitrate as part of its demonstration program in a plant with a capacity of about 15 tons per hour. The raw material requirements per ton of product are 1525 pounds of undried ammonium nitrate crystals, 360 pounds of electric-furnace phosphoric acid (80% H_3PO_4), and 110 pounds of gaseous ammonia. A small amount of sulfuric acid (50 pounds of 92% H_2SO_4 per ton of product) also is added to aid granulation. Satisfactory granulation was obtained without using iron ore or superphosphate.

A flow sheet of the process is shown in Figure 7. About one half of the phosphoric acid is preneutralized with ammonia to pH 6 in a tank 42 inches in diameter and 42 inches deep. Water is added to keep the slurry fluid enough to flow freely. The slurry, which contains about 25% water, is fed by gravity through an open-end pipe into a rotary drum mixer 7 feet in diameter by 8 feet long and rotating at 8 r.p.m. Retaining rings at each end of the mixer maintain a bed depth of 12 to 14 inches. The slurry is dispersed on top of the bed of

Table IX. Comparison of Costs of Ammonium Phosphate Nitrate and Ammonium Phosphate Urea with Conventional Fertilizers

Raw Material	Grade	Price, \$/ton	15-30-15		10-20-10		17-17-17		12-12-12	
			Ammonium Phosphate Urea		Conventional Fertilizer		Ammonium Phosphate Nitrate		Conventional Fertilizer	
			Lb./ton	\$/ton	Lb./ton	\$/ton	Lb./ton	\$/ton	Lb./ton	\$/ton
Phosphoric acid	75% H_3PO_4	76.00	1104	41.95	625	23.75
Superphosphate										
Concentrated	46% P_2O_5	60.00	654	19.62	300	9.00
Ordinary	20% P_2O_5	22.00	535	5.89	537	5.91
Potassium chloride	60% K_2O	35.00	500	8.75	333	5.83	567	9.92	400	7.00
Ammoniating solution										
U-C	45.5% N	62.24	669	20.82
X	41% N	56.48	495	13.98	494	13.95
Z-7	41.4% N	56.99	826	23.53
Sulfuric acid	93% H_2SO_4	23.00	75	0.86	112	1.29	162	1.86
Ammonium sulfate	20.5% N	38.00	195	3.71
Kaolin		12.00	80	0.48	44	0.26
Filler		4.00	27	0.05
Total raw materials cost				72.05		46.18		58.75		41.43
Operating cost				7.10		6.00		7.10		6.00
Bags				2.80		2.80		2.80		2.80
Freight (100 miles)				3.50		3.50		3.50		3.50
Sales cost				3.00		3.00		3.00		3.00
Delivered cost				88.45		61.48		75.15		56.73
Delivered cost per unit				1.47		1.54		1.47		1.58

ammonium nitrate crystals and recycle fines by an air jet impinging on the falling stream. The sulfuric acid and the remainder of the phosphoric acid are fed on top of the bed through separate distributors. The material from the mixer is discharged into a rotary ammoniator-granulator, 8 feet in diameter by 12 feet long, which rotates at 12 r.p.m. It is divided into a 3-foot ammoniating section and a 9-foot granulating section by a 12-inch retaining ring. There also is a 12-inch retaining ring at the feed end. Ammoniation and agglomeration occur in the ammoniating section where ammonia is added through a drilled pipe under the bed. The agglomerates are hardened in passing through the granulating section.

The granules are dried to a moisture content of about 0.3% in a cocurrent rotary dryer. The discharge from the dryer (220° F.) is screened at 6 and 16 mesh. The oversize is crushed in a chain mill and returned to the dryer. The fines, estimated to be 60 to 70% of the throughput, are recycled to the ammoniator. The product is passed through a rotary cooler and coated with 3% by weight of a calcined fuller's earth. The product is shipped in bulk or in bags. Typical analysis of the plant product is given in Table X.

In earlier operation, the preneutralizer was not used. The first drum was divided into a 5-foot mixing section and a 3-foot ammoniating section using a 14-inch retaining ring. Ammonium nitrate crystals, recycle fines, phosphoric acid, and sulfuric acid were mixed in the first section; ammoniation and granulation occurred in the second section. There was a considerable amount of caking in

Table X. Typical Analysis of Plant Products

Chemical Composition, Wt. %						Screen Analysis, Cumulative, % Retained on Tyler Screen					
N		P ₂ O ₅			Water-insoluble	Moisture	6	8	10	16	20
Total	NH ₃	Total	W. S.	SO ₃							
30.4	17.2	10.2	10.2	2.0	3.4	0.35	3	30	86	97	98

the ammoniator. With the preneutralizer, the amount of caking was reduced substantially. Also, the product has a higher degree of ammoniation (7.5 vs. 5.5 pounds of NH₃ per unit of P₂O₅), since the preneutralizer is operated in the pH range that results in crystallization of diammonium phosphate.

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TRACE ELEMENTS IN FERTILIZERS

Solubility Status of Zinc Carriers Intermixed with N-P-K Fertilizers

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The degree of water solubility of zinc, added to mixed fertilizers as basic zinc sulfate or zinc sulfate monohydrate, depends chiefly upon the pH of the fertilizer system. Ammoniated mixed fertilizers having a pH range of 4.6 to 6.1 showed a larger capacity for fixing zinc than nonammoniated fertilizers having a pH range of 3.6 to 4.2. Water-soluble zinc recovery was greater at pH 6.1 to 6.6 than at the intermediate pH levels, indicating the formation of soluble zincates. The results show that chelated zinc remains water soluble in N-P-K fertilizers which otherwise have a large capacity to immobilize free zinc ions.

INCORPORATING zinc carriers into mixed fertilizers, a procedure sometimes followed in the fertilizer industry, is recognized as an economical means of applying this element to soil (8, 12). In this practice, the zinc carrier may react with the components of the fertilizer during storage prior to use, thus affecting

the solubility, and hence the nutrient status, of the trace element. Nikitin and Rainey (9) conducted an investigation of reactions between trace elements and fertilizer salts in which zinc was limited to one carrier, applied at one rate to a single grade of mixed fertilizer, and evaluated after aging for one specified time

period. Expansion of each of these variables should provide additional useful information. The present investigation pertains to the effects of a wide variety of mixed fertilizers on the water solubility of three zinc carriers: basic zinc sulfate, zinc sulfate monohydrate, and a zinc chelate.