

Ammonium Polyphosphates from Superphosphoric Acid and Ammonia

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A highly concentrated fertilizer consisting primarily of ammonium orthophosphate and ammonium pyrophosphate was made in bench-scale tests by reaction of superphosphoric acid (76% P_2O_5) with ammonia. The products, called ammonium polyphosphates, were completely water soluble. Operating conditions used in the reaction step to produce grades such as 16-61-0 and 18-59-0 were: pressure, 25 to 300 p.s.i.; temperature, 365° to 415° F.; and retention time, 30 to 90 minutes. The molten material discharged from the reactor was granulated by mixing with recycle fines. Drying was not required, but agitation of the molten material hastened crystallization and hardening of the granules. The ammonium polyphosphates are suitable for direct application, bulk blending with other fertilizers, production of high-analysis liquid fertilizer solutions, and sequestration of impurities in liquid fertilizers made from wet-process acid.

THE DEVELOPMENT of a process for the production of superphosphoric acid (76% P_2O_5) by TVA (2, 6) resulted in a relatively new and useful material for the fertilizer industry. Superphosphoric acid has been used in the production of high-analysis superphosphate containing about 54% available P_2O_5 (3), liquid fertilizers of high concentration (2, 7), and granular mixed fertilizers of high concentration (2, 5). Another use is as a sequestrant to solubilize the impurities in the production of liquid fertilizers from wet-process phosphoric acid (8).

The advantages in its use stem from its high concentration and from the fact that about half of its P_2O_5 is present in forms other than the orthophosphate. According to Huhti and Gartaganis (1), phosphoric acid containing 76% P_2O_5 has the P_2O_5 distributed as approximately 49% orthophosphoric acid, 42% pyrophosphoric acid, 8% tripolyphosphoric acid, and 1% tetrapolyphosphoric acid.

This paper describes the bench-scale development of a process for the production of a highly concentrated ammonium polyphosphate fertilizer material from superphosphoric acid and ammonia. A typical product contained 17% nitrogen and 60% P_2O_5 . In this process, superphosphoric acid is ammoniated with anhydrous ammonia under moderate pressure in the liquid phase. The hot melt from the reactor is granulated together with recycled fines. The product, entirely water soluble, contains about half of its phosphate in a nonortho form. It can be used for direct application, to prepare bulk-blended mixed fertilizers, to make liquid fertilizers—

either alone or by the addition of potash, ammonia, or supplemental nitrogen materials—or as a sequestrant in the production of liquid fertilizers from wet-process acid. This material can be stored in bulk at a lower cost than the acid or liquid fertilizer base solution and can be transported at a lower cost.

Equipment and Operation

The initial tests of the reaction of superphosphoric acid and ammonia were carried out batchwise using a beaker as a reaction vessel and a laboratory stirrer for agitation. Gaseous ammonia was fed to the mixture through a glass tube used as a sparger. High ammonia loss suggested the need for a pressure reactor. A 2-liter, batch-type pressure reactor equipped with an agitator was then used to test the reaction at a pressure of 50 p.s.i.g. Over 7 pounds of ammonia per unit of P_2O_5 were retained, and loss of ammonia during the reaction was eliminated.

In the preliminary tests, the molten material was allowed to cool without agitation; the product, amorphous and plastic, crystallized slowly over a period of weeks. The melt crystallized rapidly when agitated during cooling. To obtain hard granules, therefore, in subsequent continuous tests a pugmill was used to provide agitation in granulating the liquid discharged from the reactor.

Figures 1 and 2 show the continuous reactor. The reactor, of 1-gallon capacity, was constructed of stainless steel (A.I.S.I. Type 316) and equipped with a turbine-type agitator and four baffles 1/2 inch wide by 11 inches high. Acid was fed from an overhead tank (25-

gallon capacity) with a reciprocating piston-type pump. The length of stroke of the piston could be varied to give the desired feed rate. The acid was fed at rates to give 10 to 30 pounds of product per hour.

Gaseous ammonia was fed through a 1/2 inch line from pressure cylinders located outside the laboratory building. Warm water was sprayed on the cylinders to obtain pressures up to about 325 p.s.i.g. as required. The ammonia was fed into the reactor through a 3/8 inch tube. The tube was closed at the end. A one-hole sparger, located near the bottom of the reactor under the agitator tip, was made by drilling a 0.052-inch hole at the end of the tube. The reactor was equipped with a pressure gage, and the rate of ammonia feed was controlled manually with a throttling valve to give the desired pressure of excess ammonia in the reactor. The temperature was measured with a thermocouple and a recording potentiometer.

Since the reaction of ammonia and superphosphoric acid was highly exothermic, it was necessary to provide cooling. Hot water was used for cooling to prevent freezing of material on the cooling coil (freezing point at about 325° F.). The coil, of 3/8 inch stainless steel (A.I.S.I. Type 316) tubing, provided 1 square foot of cooling area based on its external surface. Water was pumped through the cooling coil, discharged into a 1.5-gallon tank, and later recycled. Thus, the heat of reaction was utilized to heat the make-up water. The supply of cooling water in the tank remained at 212° F., and water was added as required to replace that evaporated.

Two electrical conductivity probes



Figure 1. Reactor for production of ammonium polyphosphate from superphosphoric acid and ammonia

(electrodes), entering from the top of the reactor, measured the level of the liquid in the reactor. The tips of the probes were $\frac{1}{2}$ inch apart vertically. Each probe and the shell of the reactor formed a conductivity circuit. The liquid in the reactor completed the circuit when it touched a probe and caused a light bulb to burn. The reactor was operated to keep the level between the two probes, as indicated by the top light being off and the other on. The level was controlled by the rate of drawoff of liquid from the bottom of the reactor by use of a $\frac{1}{4}$ -inch throttling valve.

The pugmill was 6 inches wide, 6 inches deep, and 3 feet long, equipped with two $1\frac{1}{2}$ -inch shafts with $1\frac{5}{8}$ - by 1-inch blades set on 2-inch centers along the shaft at an angle of 30 degrees to convey the material. One shaft had blades in groups of two, set 180 degrees apart around the shaft, and the other had blades in groups of three set 120 degrees apart. The ratio of rotation of the two-blade to the three-blade shaft was 3 to 2. In this way the blades intermeshed and had a cleaning action. The two-blade shaft was rotated at 90 r.p.m.

Effect of Operating Variables on Degree of Ammoniation

In the initial tests, the degree of agitation in the reactor had a significant effect on the degree of ammoniation. The reactor first was equipped with a six-blade agitator impeller $2\frac{1}{2}$ inches in diameter with blades $\frac{1}{2}$ inch wide, located one agitator diameter above

the bottom of the reactor. The agitator was rotated at 600 r.p.m., and the degree of ammoniation was only about 5 pounds of ammonia per unit of P_2O_5 . Increasing the width of the blades to 2 inches increased the degree of ammoniation to 6.3 pounds of ammonia per unit of P_2O_5 when the speed of the agitator was 600 r.p.m. The degree of ammoniation increased to 7.5 pounds of ammonia per unit of P_2O_5 when the agitator speed was increased to 1730 r.p.m. No further increase was obtained when the speed of the agitator was increased to 2130 r.p.m. (see Table I).

Temperature and pressure were related in their effects on the degree of ammoniation and the freezing point of the melt in the reactor. At pressures of 300 p.s.i.g., it was necessary to keep the temperature at $415^\circ F.$ so that the melt would be fluid; at 25 p.s.i.g., temperatures as low as $365^\circ F.$ could be used. The tests were made with an agitator speed of 2130 r.p.m. and a retention time of about 60 minutes (Table I and Figure 3).

At a reaction temperature of $415^\circ F.$ increasing the pressure from 25 to 300 p.s.i.g. increased the degree of ammoniation from 5.7 to 7.5 pounds of ammonia per unit of P_2O_5 . At a pressure of 25 p.s.i.g. increasing the temperature from 365° to $450^\circ F.$ decreased the degree of ammoniation from 7.0 to 5.3 pounds of ammonia per unit of P_2O_5 . At a reactor pressure of 25 p.s.i.g. and temperatures of 350° to $370^\circ F.$, as the retention time was increased from 30 to 90 minutes, the degree of ammoniation increased from

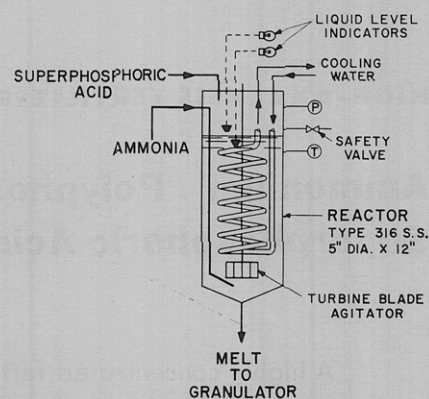


Figure 2. Detailed diagram of pressure reactor for producing ammonium polyphosphate

6.8 to 7.2 pounds of ammonia per unit of P_2O_5 .

To obtain the highest degree of ammoniation, high pressure, low temperature, and long retention time should be used; however, the physical limitation of retaining a fluid melt that can be agitated must be met in setting the conditions of operation.

Granulation

The molten material had a specific gravity of 1.6 as it was discharged through a pipe or a spray nozzle from the reactor onto a bed of recycle fines in the pugmill. Both the pipe and the spray nozzle were satisfactory, but the nozzle gave some trouble with clogging. Recycle fines at room temperature were fed to the pugmill with a disk feeder. The fines were accumulated by screening the granular material from the pugmill on hand screens. The product removed was $-6 +12$ mesh in size. The oversize particles were crushed in a roll crusher to -12 mesh and returned to the pugmill as recycle. A recycle ratio of about 3 pounds per pound of feed appeared to be satisfactory.

Properties of Product

Microscopic examination showed that the product granules were mainly crystalline material cemented together by an amorphous phase. Some of the crystalline material could not be identified from present microscopic data. Other crystalline materials were monoammonium orthophosphate, tetrammonium pyrophosphate, and triammonium pyrophosphate monohydrate. The phosphate was divided about equally as ortho and nonortho phosphate.

Some products were tested in the greenhouse for their fertilizer value. The P_2O_5 in solid ammonium polyphosphate was as effective as the P_2O_5 in diammonium phosphate and slightly more effective than the P_2O_5 in superphosphate. The nitrogen was as effective as the nitrogen in ammonium sulfate.

The granules were subjected to hygroscopicity tests—i.e., exposure to air at 86° F. and 70% relative humidity for 1 hour. The gain in weight due to moisture absorption was about 4%. Ammonium nitrate prills similarly exposed gained about 10% in weight.

The product was hard, tough, and free flowing when made. Accelerated caking tests indicated that it should store satisfactorily. In regular bag-storage tests carried out in 12-bag stacks in an unheated, ventilated building, the product was in good condition after 1 month of storage, but was caked after 3 months. Microscopic studies showed some deformation of the particles when in contact with each other; at these points, there had been some growth and interlocking of very fine crystals of mono-ammonium phosphate. Other tests showed that caking was significantly decreased by dusting the product with 1% by weight of a conditioning agent such as calcined dolomite. The caking problem is being studied further in pilot-plant work.

Granular ammonium polyphosphate was tested for compatibility with ammonium nitrate, potassium chloride, urea, ammonium sulfate, triple superphosphate, and high-analysis superphosphate. The mixtures were stored in bottles, subjected to accelerated caking tests, and checked for odors and other signs of reactions. Ammonium polyphosphate was compatible with all materials except triple superphosphate and high-analysis superphosphate. With triple superphosphate, and to a lesser extent with high-analysis superphosphate, there was a tendency to cake. A conditioner, such as 2% of calcined dolomite incorporated in the mixture, eliminated caking.

A 10-34-0 grade base solution similar to that being produced from superphosphoric acid, ammonia, and water was made by dissolving granular ammonium polyphosphate having the desired N to P₂O₅ ratio (7.1 lb. NH₃ per unit of P₂O₅) in water. This solution did not salt out at 32° F. As when liquid fertilizers are produced from conventional solid materials by cold mixing procedures, the rate of solution of the ammonium polyphosphate was slow because of the negative heat of solution, but could be increased by supplying heat, using hot water, or adding some acid and ammonia to utilize the heat of reaction. When granular material having a lower degree of ammoniation (16-60-0 grade; 6.5 lb. NH₃ per unit of P₂O₅) was used and ammonia added to give the N to P₂O₅ ratio required for a 10-34-0 grade, the heat liberated by ammoniation resulted in complete dissolution in about 5 minutes.

In tests of the production of liquid fertilizers by ammoniating wet-process phosphoric acid, the addition of solid

Table I. Tests of the Production of Ammonium Polyphosphates—Effects of Operating Variables on Degree of Ammoniation

| Agitator Speed, ^a R.P.M. | Temp., ° F. | Pressure, P.S.I.G. | Retention Time, Min. | Product Composition, % | | Lb. NH ₃ / Unit P ₂ O ₅ |
|--|----------------|-----------------------|-------------------------|------------------------|-------------------------------|---|
| | | | | N | P ₂ O ₅ | |
| EFFECT OF AGITATION | | | | | | |
| 600 ^b | 370 | 140 | 60 | 12.9 | 64.2 | 4.9 |
| 600 | 350 | 130 | 63 | 15.9 | 61.5 | 6.3 |
| 1020 | 375 | 200 | 59 | 16.7 | 62.0 | 6.5 |
| 1520 | 400 | 200 | 62 | 17.7 | 60.4 | 7.1 |
| 1730 | 390 | 200 | 63 | 18.2 | 59.2 | 7.5 |
| 2130 | 395 | 200 | 55 | 18.0 | 59.8 | 7.3 |
| EFFECT OF PRESSURE | | | | | | |
| 2130 | 415 | 25 | 60 | 14.4 | 61.8 | 5.7 |
| 2130 | 415 | 100 | 60 | 15.7 | 61.4 | 6.2 |
| 2130 | 415 | 150 | 60 | 16.1 | 61.4 | 6.4 |
| 2130 | 415 | 175 | 60 | 16.8 | 61.1 | 6.7 |
| 2130 | 415 | 200 | 60 | 18.2 | 59.8 | 7.4 |
| 2130 | 415 | 300 | 60 | 18.3 | 59.2 | 7.5 |
| EFFECT OF TEMPERATURE | | | | | | |
| 2130 | 365 | 25 | 60 | 17.3 | 59.8 | 7.0 |
| 2130 | 380 | 25 | 60 | 16.1 | 61.1 | 6.4 |
| 2130 | 395 | 25 | 60 | 15.9 | 61.5 | 6.3 |
| 2130 | 410 | 25 | 60 | 14.5 | 62.5 | 5.6 |
| 2130 | 450 | 25 | 60 | 13.6 | 62.7 | 5.3 |
| EFFECT OF RETENTION TIME | | | | | | |
| 2130 | 350 | 25 | 30 | 17.0 | 60.6 | 6.8 |
| 2130 | 365 | 25 | 60 | 17.3 | 59.8 | 7.0 |
| 2130 | 370 | 25 | 90 | 17.8 | 59.7 | 7.2 |

^a Agitator was 2.5 inches in diameter and 2 inches wide except where noted.

^b Agitator, 2.5 inches in diameter and 1/2 inch wide.

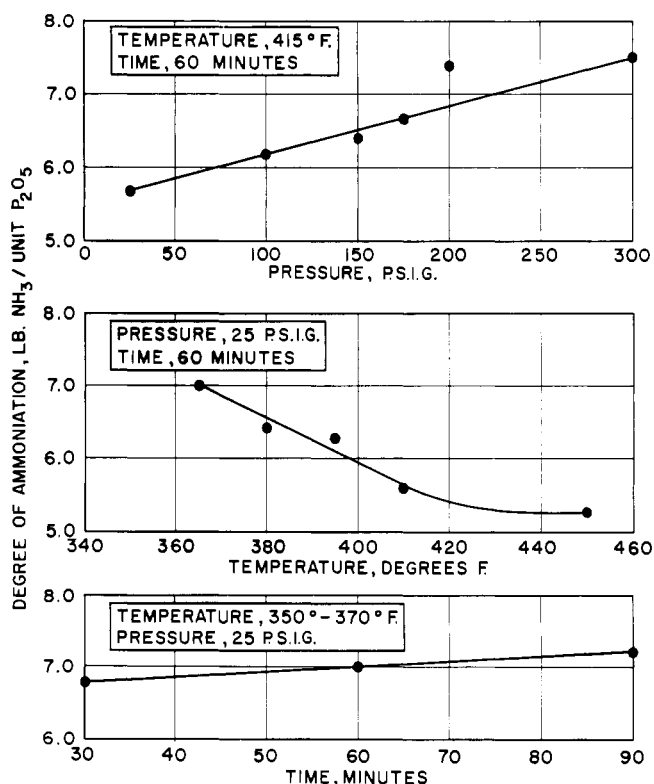


Figure 3. Effect of operating variables on degree of ammoniation

ammonium polyphosphate in amounts equal to 20 to 30% of the P_2O_5 in the solution effectively sequestered the impurities which would have precipitated from the acid. The solutions (8-24-0 and 6-18-6) were free of solids.

Discussion

Bench-scale production of ammonium polyphosphate yielded a granular product requiring no drying and having a plant-food content of 77 to 78%, which is higher than in any combination fertilizer known at present.

The use of moderate pressure for the reactor eliminates the need for a scrubber to recover ammonia. Further studies are being carried out in pilot-plant scale equipment where the ammonia feed system was made automatic by use of a pressure regulating valve in the feed line. The temperature and level control could be made automatic also, giving completely automatic control of the reactor.

Use of Wet-Process Phosphoric Acid

Exploratory studies have been started on the production of ammonium polyphosphates from highly concentrated wet-process phosphoric acid (about 72% P_2O_5) and ammonia. The production of this acid from merchant-grade acids

is described by Scott (4). In general, the ammonium polyphosphates were produced from the highly concentrated phosphoric acid by the same operating procedure used in tests with superphosphoric acid.

Only one acid, produced from Florida rock, has been tested thus far. It had the following analysis:

| Acid analysis, % by weight | | | | | |
|----------------------------|----------------|-----|--------|-----------|-----------|
| Total P_2O_5 | Ortho P_2O_5 | F | SO_3 | Al_2O_3 | Fe_2O_3 |
| 71.7 | 36.2 | 0.3 | 2.5 | 1.3 | 1.6 |

In the first tests, an unsatisfactory product was obtained at 25 p.s.i.g. and 375° F. The degree of ammoniation was only about 6.2 pounds of ammonia per unit of total P_2O_5 ; the product was very hygroscopic and caked severely in accelerated caking tests. A hard, less hygroscopic product was obtained when the pressure was increased to 300 p.s.i.g. and the temperature was 425° F. At this reactor pressure, 6.5 pounds of ammonia per unit of total P_2O_5 were fixed and the product had a grade of 15-58-0. The degree of ammoniation and product grade were less than obtained under the best operating conditions with superphosphoric acid (7.4 lb. NH_3 per unit of P_2O_5 and a grade of 18-59-0).

Studies of the production of ammonium polyphosphate from highly concentrated wet-process acids are being continued.

Acknowledgment

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FERTILIZER MATERIALS

Melting Points in Orthophosphoric Acid-Pyrophosphoric Acid System

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FERTILIZER TECHNOLOGISTS recently saw the introduction of superphosphoric acid (17, 18) as a material equivalent to about 105% orthophosphoric acid in the manufacture of solid (13) and liquid (19) fertilizers. Its phosphoric oxide content (about 76%) places superphosphoric intermediate in composition between orthophosphoric acid (72.4% P_2O_5) and pyrophosphoric acid (79.8% P_2O_5). Occasions for its storage and shipment in winter lead to interest in the freezing points of compositions in the ortho-pyro range.

The early work with superphosphoric acid as a fertilizer material demonstrated qualitatively its outstanding characteristics of fluidity, including its persistence as a liquid when strongly supercooled over long periods, even when seeded. Although advantageous in a practical way, these characteristics introduced formidable difficulties in the measure-

ments presented here as a basis for a melting-point diagram of the orthophosphoric-pyrophosphoric region of the system phosphoric oxide-water.

Methods

Solid phosphoric oxide was dissolved in orthophosphoric acid (reagent grade) to yield a stock solution which was filtered, then stirred 2 hours at 135° C. to promote equilibrium among the species of phosphoric acid. This solution (81% phosphoric oxide) was diluted to make secondary stock solutions of integral concentrations which were blended to yield specific gross concentrations for the measurements.

Ten-milliliter charges of the various acid compositions, seeded with ortho or pyro crystals as appropriate, were sealed in 12-mm. borosilicate glass tubes and

stored at room temperature or at 7° C. until crystallization was essentially complete. In the absence of seed, compositions with melting points below room temperature were difficult to crystallize; rapid cooling by immersion in solid carbon dioxide or liquid nitrogen produced glasses instead of crystals.

The tubes of crystals were mounted on a rocker in a water bath and oscillated through an arc of 110°—enough to wet the walls with liquid phase as the crystals melted. By means of an electronic controller, the temperature was raised in steps of 1° or 2° C. until liquid phase appeared, then at a rate of 0.1° C. per day until the proportion of solid phase was 5% or less, and finally at a rate of 0.05° C. per day to disappearance of crystals, and the temperature then was taken as the melting point. Temperatures were read on a Beckmann thermometer that was checked against a