

least 1 hour of exposure, and many of them remained drillable after a much more severe exposure than would be normally expected in farm practice.

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FERTILIZER TECHNOLOGY

Production of Diammonium Phosphate by Continuous Vacuum Crystallization

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Diammonium phosphate was produced on demonstration scale in a vacuum crystallizer. The product was a coarse crystalline material containing 21% of nitrogen and 53% of phosphorus pentoxide. The process, developed earlier in pilot-plant work, consisted of feeding ammonia and furnace-grade phosphoric acid into a vacuum crystallizer. The crystal slurry was centrifuged and the crystals were dried. The mother liquor was maintained on the acid side, pH 6.5, which resulted in a low partial pressure of ammonia over the solution so that recovery of ammonia from vapors was unnecessary. The process was carried out in a vacuum crystallizer adapted from the production of crystalline ammonium nitrate. Only minor changes were required.

DIAMMONIUM PHOSPHATE as a fertilizer offers the advantages of high concentration of plant food (21% of nitrogen, 53% of phosphorus pentoxide) and favorable agronomic and physical properties. It can be used for direct application or for preparation of high-analysis fertilizers by either dry-mixing (6) or granulation (2) techniques. As diammonium phosphate is completely soluble in water, it can be used in irrigation systems and in liquid fertilizers.

The pilot-plant development for the production of diammonium phosphate fertilizer in a saturator or vacuum crystallizer from anhydrous ammonia and electric-furnace phosphoric acid has been described by Thompson and associates (7). A modification of the vacuum crystallization process that permits the use of impure, wet-process phosphoric acid has been described by Houston and coworkers (3).

In view of the potential advantages and uses cited above, TVA decided to produce diammonium phosphate from electric-furnace phosphoric acid as a part of its program for introducing and demonstrating the use of new and improved forms of fertilizer materials.

The purpose of this paper is to describe the diammonium phosphate production process as it was carried out in the TVA plant. Although the use of one type of crystallizer is described,

other types could be used satisfactorily, as shown by pilot-plant work (7). Crystallizers are in use currently in the fertilizer industry for making ammonium sulfate and other materials. The alternate use of such crystallizers for diammonium phosphate would provide flexibility for adjusting to changing market conditions.

Description of Process

The diammonium phosphate production facilities were located in the TVA ammonium nitrate plant. Much of the equipment that was to be used to produce diammonium phosphate originally was a part of the ammonium nitrate plant and now may be used in either process.

The TVA ammonium nitrate vacuum crystallization plant has been described by Saeman, McCamy, and Houston (5). It has five continuous vacuum crystallizers designed and fabricated by the Struthers-Wells Corp. Each unit has a production capacity of about 5 tons of ammonium nitrate per hour. The five crystallizers, which are operated in parallel, use a common surge tank and discharge to a common tank from which the crystal slurry is fed to two of three continuous centrifuges. One of the centrifuges has served as a stand-by.

The changes that were required to pre-

pare for the production of diammonium phosphate consisted of isolating one of the crystallizers from the ammonium nitrate circuit, installing piping for feeding ammonia and phosphoric acid, providing a separate surge tank, and installing drying and screening equipment. The stand-by centrifuge was used for dewatering the crystal slurry.

A flow sheet of the process is shown in Figure 1. Anhydrous gaseous ammonia, at 25 pounds per square inch of pressure, and electric-furnace phosphoric acid, about 78% concentration, were fed continuously to the crystallizer. The acid was fed at a predetermined rate and the ammonia was fed at such a rate as to maintain the pH of the mother liquor at about 6.5. The operating temperature was maintained at 125° F. Thompson and associates (7) found that, under these conditions, diammonium phosphate crystallized from the mother liquor with very little loss of ammonia in the vapors.

If 54% phosphoric acid had been used, vaporization of the water in the acid would have dissipated the heat liberated by the reaction of 2 moles of ammonia with 1 mole of phosphoric acid (7). With the more concentrated acid, water was added to the system to aid in dissipating the heat. This water was used to dissolve fines and the resulting solution was added to the surge tank (see Figure 1).

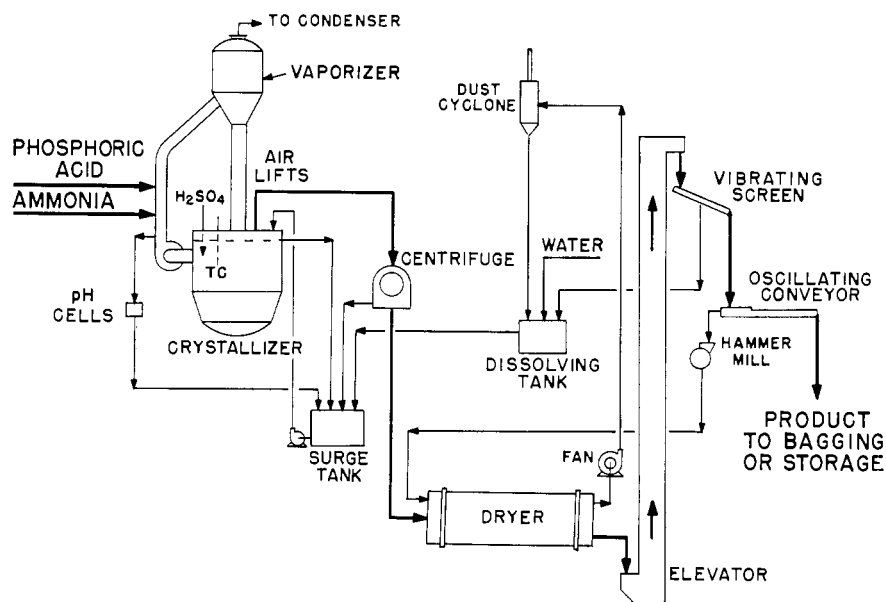


Figure 1. Diammonium phosphate by vacuum crystallization

Crystal slurry was removed continuously from the crystallizer; the crystals were dewatered by centrifuging and then were dried and screened. The mother liquor from the centrifuge was returned to the surge tank.

Material and energy requirements for the plant are shown in Table I and operating data are shown in Table II.

Crystallization. The crystallizer consisted essentially of a suspension tank that was open to the atmosphere, a vaporizing chamber under vacuum, a barometric leg, and a recirculating leg with a pump for circulating the liquor. The suspension tank was 16 $\frac{1}{2}$ feet in diameter and 20 feet high. The vaporizer was 9 feet in diameter by 16 $\frac{2}{3}$ feet high. The holdup volume of the system was about 24,000 gallons. Two air lifts removed crystal slurry from the suspension tank continuously for centrifuging. The crystallizer and accessories were constructed of American Iron and Steel Institute (A.I.S.I.) Type 430 stainless steel.

The recirculation pump, driven by a 50-hp. motor, had a capacity of about 7000 gallons per minute. The recirculation leg was 2 feet in diameter. Spargers were installed in the recirculation leg 4 feet above the pump outlet because the velocity of flow was high at this point and good mixing was obtained. The sparger for acid consisted of a 2-inch Type 316 stainless steel pipe, closed at the end and provided with a slot 0.75 inch wide and 3 inches long. The slot faced downward opposed to the flow of liquid from the recirculation pump. The ammonia sparger, located 6 inches beneath the acid sparger, consisted of a 2-inch Type 316 stainless steel pipe that was closed at the end and drilled with 87 0.25-inch-diameter holes that faced upward. The recirculation pipe was lined with 16-gage Type 316 stainless steel starting at the spar-

gers and extending upward for a total height of 6 feet. The lining was precautionary with regard to corrosion from possible localized high acidity in the sparger section.

The vacuum system for the crystallizer consisted of a multispray condenser and two ejectors with an intercondenser and was constructed of mild steel and cast iron with Type 316 stainless steel nozzles in the ejectors. The system had a capacity of 7000 pounds of water vapor per hour at a solution temperature of 125° F. and a pressure of about 3 inches of mercury, absolute.

The surge tank was 9 feet in diameter by 8 feet high and was fabricated from Type 430 stainless steel. It received a constant overflow from the crystallizer suspension tank, solution from the fines-dissolving tank, liquor from the centrifuge, and sampling streams from the crystallizer. A 140-gallon per minute centrifugal pump returned the slurry from the surge tank to the crystallizer suspension tank. A turbine impeller driven by a 10-hp. motor kept crystals from settling out and served to mix the several incoming solutions. The liquid level in the surge tank was used to regulate the rate of water addition to the fines dissolving tank.

The primary control of the process was based on pH of the mother liquor, which was measured by means of continuous sampling. The sample line was connected to the recirculation line below the spargers (Figure 1). A positive pressure at that point served to move the sample solution continuously through two glass electrode pH cells, which were connected to a recorder located in a control room. The sample discharged from the cells to the surge tank. The flow of slurry to each electrode cell was controlled independently. The pH circuits between the two sets of electrodes and the recorder were interchangeable to allow cross checking and washing of the electrodes in place. Owing to the buffered nature of the crystallizing system, the pH of the mother liquor was controlled satisfactorily by manual control of the ammonia flow. Orifice meters were installed both on the acid line and on the ammonia line. A small flow of water or steam was admitted intermittently to the ammonia line to prevent plugging of the sparger.

The crystallizer was operated at a temperature of 125° F., which was regulated automatically by control of the vacuum. A thermostat regulated the rate of flow of water to the spray condenser, which in turn controlled the vacuum. A recorder in the control room recorded the temperature of the solution, which was measured by a thermocouple in the suspension tank.

The suspension density was maintained at about 30% crystals by volume, by regulating the rate of removal of crystals

Table I. Material and Energy Requirements for Producing 1 Ton of Diammonium Phosphate

Phosphoric acid (78% H ₃ PO ₄), ton	0.95
Ammonia, ton	0.26
Water, make up, gal.	86
Steam to ejectors (125 lb./sq. inch gage), lb.	100
Water to condensers, gal.	6000
Steam to dryer (125 lb./sq. inch gage), lb.	185
Electric power, kw.-hr.	30

Table II. Operating Data

(Average of 8-month period)

Crystallizer temperature, ° F.	125
Crystallizer vacuum, inches Hg absolute	3
Mother liquor pH	6.5
Mole ratio NH ₃ :H ₃ PO ₄ in mother liquor	1.7
SO ₃ , % by weight in mother liquor	5.3
Suspension density, % by volume	30
Specific gravity of mother liquor (125° F.)	1.31
Crystallization rate, tons/operating hr.	3.0
Moisture in centrifuged product (dryer feed), %	2.3
Dryer inlet air temperature, ° F.	300
Dryer discharge air temperature, ° F.	155
Dryer product temperature, ° F.	150
Particle size of dryer product (Tyler screen series), %	
+20 mesh	43.0
-20 +32 mesh	30.7
-32 mesh	26.3
Particle size of screened product, %	
+20 mesh	51.6
-20 +32 mesh	33.2
-32 mesh	15.2
Production rate of screened product, tons/operating hr.	2.5
Analysis of screened product, %	
N	20.9
P ₂ O ₅	53.7
Moisture	0.08
Bulk density of screened product, lb./cu. ft.	56

by the air lifts. Satisfactory operation also was obtained with 40% suspension. The suspension density was measured every hour by filtering a sample of the crystal slurry.

The crystallizer was operated with a circulating suspension, as in the case of ammonium nitrate (5). However, the fine salt separator in the crystallizer was not used. Instead, the dried crystals were screened and the fines were dissolved in the water added to the system.

Diammonium phosphate crystallizes from pure solutions in the form of plates. The shape of the crystals can be modified to almost cubical by the presence of a small amount of sulfate in the mother liquor. A photograph of the two types of crystals is shown in Figure 2. To produce the sulfate-modified type of crystal, sulfuric acid was added at the inlet of the crystallizer recirculation pump at intervals of 8 hours. About 8 pounds of 66° Baumé sulfuric acid per ton of diammonium phosphate produced was adequate to maintain the sulfur trioxide concentration in the required range, between 3 and 8% of the mother liquor by weight, which was somewhat below saturation. The sulfur trioxide content of the product was about 0.3%.

The crystallization rate used in the plant averaged about 2 pounds of crystals per operating hour per cubic foot of solution. Although the effect of rate on crystal size was not investigated in the plant because of limitations of accessory equipment, it was investigated in a pilot-plant crystallizer described in an earlier paper (3). The results of the pilot-plant tests (Table III) show that increasing the rate resulted in a significant decrease in crystal size. The lowest rate used in the pilot plant, 4 pounds of crystals per hour per cubic foot of solution, resulted in a slightly lower percentage of plus 20-mesh crystals than obtained in the plant at the 2-pound rate (Table II). The addition of sulfate had no significant effect on the screen analysis (Table III), as the sulfate only increased the thickness, leaving the other two dimensions relatively unchanged.

Centrifuge. Crystal slurry from the air lift flowed by gravity to a Baker Perkins Co. Type S continuous, horizontal-basket centrifuge. The basket was 48 inches in diameter and rotated at a

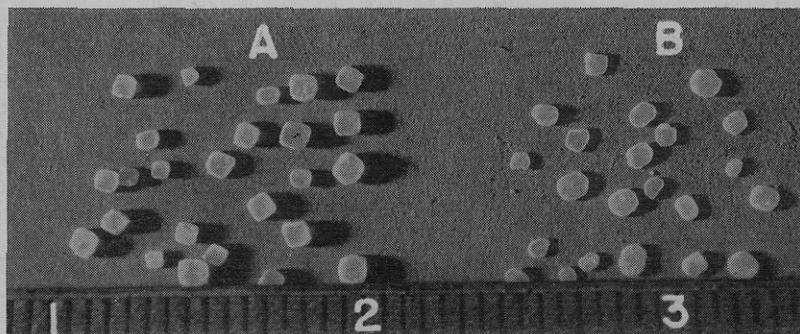


Figure 2. Diammonium phosphate crystals made (A) with and (B) without addition of sulfate to crystallizer

speed of 370 r.p.m. The centrifuge was constructed of Type 430 stainless steel with the exception of the basket, which was made of Type 316 stainless steel, with 0.012- to 0.015-inch wedge slots. The depth of the crystal bed was 1.5 inches. The centrifuged crystals, containing 2 to 3% moisture, were discharged to a 16-inch belt conveyor which fed the dryer. The centrifuge liquor, containing 3 to 5% crystals, was discharged to the surge tank.

Dryer. Drying was carried out in a rotary dryer with a cocurrent flow of hot air. The dryer, which was made of plain steel, was 4 feet 5 inches in inside diameter by 38 feet 10 inches long. It was driven at 6.6 r.p.m. by a 25-hp. gear motor. The shell and the wind box at the feed end were insulated with 2 inches of slag wool. The first 3 feet of the shell had six 8-inch advancing flights; the next 8 feet had twelve 6-inch radial flights; and the next 23 feet 10 inches had twelve flights made from 6-inch lightweight pipe split in half. The remaining 4 feet had no flights. A forced-draft fan and an induced-draft fan, each with a 15-hp. motor, moved the air through the dryer to a cyclonic dust collector, which had a 3.5-foot diameter body. The air velocity in the dryer was about 5 feet per second.

The temperature of the air to the dryer was limited to about 300° F., as it was heated with 125-pound steam, which was the most convenient source of heat.

The temperature of the product from the dryer was maintained at 140° F. or higher to ensure a product with not more than 0.1% moisture. Under these conditions, the throughput was limited

to about 5 tons per hour, which resulted in a net production rate of 4 tons per hour. The retention time in the dryer was about 10 minutes. The production rate could have been increased by increasing the temperature of the air used for drying. In pilot-plant tests, there was no significant loss of ammonia when the product temperature was 200° F.

Dry Material Handling. The product from the dryer discharged to a bucket elevator which discharged to a vibrating screen (28 mesh, Tyler) for the removal of fines. However, the screen was overloaded, and only about half of the fines were removed. The product that passed over the screen was discharged to an oscillating pan conveyor 4 inches deep by 12 inches wide by 65 feet long. A scalping screen (4 mesh) for removing lumps was incorporated in the first 10 feet of this conveyor. The conveyor carried the product to a bagging machine, to a chute that fed a box-car bulk loader, or to a hopper car for transportation to a bulk-storage building. Multiwall paper fertilizer bags having one asphalt-laminated ply were used when the product was bagged.

The small amount of oversize lumps (about 1%) from the scalping screen was crushed in a hammer mill and returned to the dryer. Fines from the dust collector and from the vibrating screen (about 20%) were discharged by gravity through chutes to dissolving tanks.

Dissolution of fines was accomplished in two steel tanks in series provided with agitators. The first was a 300-gallon tank, and the second was a 130-gallon tank. Fines and water were added to the first tank. A steam sparger was provided in the first tank to aid in dissolving the crystals. The solution flowed by gravity from the first tank to the second and to the surge tank of the crystallizer.

Product. Chemical and screen analyses of the product are shown in Table II. The chemical analysis was very uniform and ranged only from 20.8 to 21.0% of nitrogen and 53.5 to 53.9% of phosphorus pentoxide. The moisture content ranged from 0.05 to 0.1% as

Table III. Effect of Crystallization Rate on Screen Size of Crystals

(Pilot-plant tests)

Crystallization Rate, Lb./(Hr.) (Cu. Ft. Soln.)	Particle Size (Tyler Screen Series), %		
	+20 mesh	-20 + 35 mesh	-35 mesh
4	38.6	46.2	15.2
4 ^a	38.8	46.4	14.8
8	6.8	42.3	50.9
24	1.3	13.1	85.6

^a Sulfate added; 10% SO₃ maintained in mother liquor.

determined with Karl-Fischer reagent (4). The vacuum desiccator method for moisture (7) was not used because equilibrium was not reached in the prescribed 16 hours, presumably because of loss of ammonia. Silverberg and Heil (6) have described the storage properties of bulk and bagged diammonium phosphate.

Losses. Losses of ammonia and phosphorus pentoxide from the crystallizer were measured by analyzing a continuous sample of the effluent from the barometric leg of the spray condenser. The rate of flow of the effluent was measured with an orifice meter. Blank determinations for nitrogen and phosphorus pentoxide were made on the cooling water to the condenser. Losses measured in this way were 2.3% of the ammonia and negligible amounts of phosphorus pentoxide. The low phosphorus pentoxide loss indicated that very little entrainment occurred in the vaporizer. The losses reported here are considered to be acceptable; however, the ammonia loss could be reduced further by lowering the operating pH or by lowering the operating temperature. More care would be necessary in using a lower pH, as monoammonium phosphate crystallizes when the pH is below about 5.8 (7). The only limitation on lowering the temperature would be the capacity of the evacuating system.

Impurities. After several weeks of operation, the mother liquor, which originally was clear and colorless, became dark and cloudy with impurities that were in the phosphoric acid. The con-

centration of insoluble impurities in the mother liquor varied from 0.1 to 1.0% by weight. A chemical analysis of a sample of filtered, washed, undried impurities from the mother liquor showed: 14.0% of phosphorus pentoxide, 9.3% of calcium oxide, 6.0% of silicon dioxide, 1.6% of aluminum oxide, 0.3% of ferric oxide, 1.6% of fluorine, and 57.0% of water. The insoluble impurities were discharged from the crystallizer by retention on the crystals and had no effect on operation.

Discussion

The over-all operation of the plant was exceptionally trouble-free. Close control of feed proportions was not required because diammonium phosphate crystallizes from a mother liquor that may vary widely in composition. No difficulty with freezing of material in pipelines was experienced because of the favorable temperature-solubility relationship of diammonium phosphate. Ammonia losses were controlled easily without recovery equipment. The crystals formed were strong and did not break in the centrifuge and dryer. The crystals dried quickly, and little caking occurred in the dryer. The product was free flowing and easily handled with bucket elevators, belt conveyors, vibrating conveyors, and screw conveyors. No dust or fume nuisance was created.

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FERTILIZER STORAGE

Storage Properties of Diammonium Phosphate Alone and in Admixture with Other Fertilizer Materials

DIAMMONIUM PHOSPHATE FERTILIZER as produced by TVA (2) in its demonstration plant is a crystalline material containing 21.0% nitrogen, 53.7% phosphorus pentoxide, and less than 0.1% moisture. It is produced from anhydrous gaseous ammonia and electric-furnace phosphoric acid in a vacuum crystallizer, and a small amount of sulfuric acid is added during crystallization to change its crystal shape from plate to almost cubical. It is relatively non-hygroscopic, having a critical humidity of about 83% at 86° F. About 85% of the product is larger than 32 mesh in size.

Because of its relatively low hygroscopicity and its very low moisture con-

centration, it was first thought that the product would not cake in storage. However, bag set and caking did occur to some degree even though the product was stored in multiwall paper bags having moisture-resistant plies; actually, light cementing of the crystals occurred. Tests were made to determine the storage properties of crystalline diammonium phosphate and to identify conditioning agents that would prevent caking.

Bag Storage of Diammonium Phosphate

The material to be tested was bagged in five- and six-ply paper bags having one- and two-asphalt laminated plies, respectively. Bags filled with 80 pounds

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of the material were stored for periods of up to 9 months in stacks 12 bags high. The storage area was in a large, unheated warehouse of hollow tile construction with a concrete floor. The windows of the building were open. Each test stack rested on a sand-filled dummy bag placed on a wooden platform. Three or four test stacks were used for each product. After storage periods of 1, 3, 6, and 9 months, the bags in positions 11 and 12 from the top were removed from one stack and inspected. The bags in positions 1 through 10 usually were not inspected, and in many cases dummy bags were used in these positions. At the time of inspection, the degree of bag set and the