

# Separation of Ammonium Phosphate from Ammonium Nitrate in Sulfate Recycle Nitric Phosphate Process

Owen W. Livingston, Glenn M. Blouin,\* and John G. Getsinger

Essentially complete separation of phosphate from ammonium nitrate in the gypsum-crystallizer filtrate from the sulfate recycle process was accomplished in continuous bench-scale equipment with a two-stage ammoniation procedure. In the first stage (pH 5.7; boiling; retention, 1 hr) the iron, aluminum, and calcium impurities were precipitated and formed into easily filterable agglomerates. This slurry then was ammoniated further (pH 9.5, 100° F) to precipitate the phosphate as triammonium phosphate trihydrate, which later was decomposed

with heat to diammonium phosphate (N-P-K, 18-20-0; N-P<sub>2</sub>O<sub>5</sub>-K<sub>2</sub>O, 18-46-0). Ammonia from the decomposition step would be recycled to the first stage. The ammonium nitrate filtrate can be processed to solid (33-0-0) or can be combined with ammonium phosphate to produce a variety of grades. The ability to carry out this separation adds great flexibility to the original process, which provides only for a single product, which has a high N-P ratio (28-6-0; N-P<sub>2</sub>O<sub>5</sub>-K<sub>2</sub>O, 28-14-0).

In the sulfate recycle nitric phosphate process for manufacture of N-P fertilizer, phosphate rock is acidulated with nitric acid and the resulting acidulate is reacted with recycled ammonium sulfate solution to precipitate calcium as calcium sulfate dihydrate (gypsum). When the gypsum is filtered off, the filtrate contains principally ammonium nitrate and phosphoric acid with small amounts of iron and aluminum compounds. Further processing of this solution to a solid by ammoniation and granulation results in a product of 28-6-0 (N-P<sub>2</sub>O<sub>5</sub>-K<sub>2</sub>O grade, 28-14-0) (Blouin *et al.*, 1970). The chief objection to this product is its high N:P ratio. For many marketing situations it would be more desirable to have two products: one a low N:P ratio, and the other ammonium nitrate.

Methods have been described by Strelzoff and Roberts (1954), Strelzoff and Dell (1968), and McFarlin and Brown (1968) for separating nitrate from phosphate so that flexibility in product grades can be achieved. The Strelzoff process involved the ammoniation of the gypsum-crystallizer filtrate to pH 3.5 with concentration to give a precipitate of monoammonium phosphate which was removed by filtration. In this process, separation of the phosphate and nitrate was incomplete. In the McFarlin process, the filtrate was concentrated at low pH to cause crystallization of ammonium nitrate, which was removed by centrifugation. The ammonium nitrate was diluted with phosphatic impurities and retained mother liquor since the cake could not be washed.

An alternate method for separation of nitrate and phosphate, which was described briefly by Blouin *et al.* (1970), has been studied further by TVA in continuous-type bench-scale equipment with objectives of obtaining a high degree of separation of nitrate and phosphate and of overcoming the problem of poor filtration rates due to the presence of finely divided precipitates of impurities. A flowsheet of the process is shown in Figure 1.

In this process, essentially complete separation of the phosphate from the gypsum-crystallizer filtrate was achieved by ammoniation to pH 9-10 in the two-stage ammoniator for crystallization of the phosphate as triammonium phosphate trihydrate [(NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O, TAP], which later was decomposed by heating to form diammonium phosphate.

The phosphate was precipitated as TAP because it is considerably less soluble in this form than as diammonium phosphate or monoammonium phosphate (Flatt *et al.*, 1955). Poor filterability was overcome through the use of the two-stage ammoniation; the first stage was carried out at pH 5.7 and 220° F (boiling) to precipitate the iron, aluminum, and calcium impurities and form them into agglomerates that filtered readily with the TAP crystals precipitated in the second stage at pH 9.5 and 95° F. The TAP was filtered and washed with ammonium hydroxide to remove ammonium nitrate and then heated to evolve ammonia and form an 18-20-0 (18-46-0) grade ammonium phosphate product similar to wet-process diammonium phosphate.

The ammonium phosphate products can be used in direct application, as an intermediate in the production of compound N-P-K products, and in bulk blending with other fertilizer materials except urea. The reaction of urea with the residual nitrate in the product not removed by washing probably would result in a mixture of very low critical relative humidity and cause the blend to have poor storage properties.

The filtrate from the second ammoniation stage, which contains ammonium nitrate and small amounts of ammonium phosphate and ammonium sulfate, can be concentrated and processed into a solid containing about 33% nitrogen. The ammonium nitrate could also be returned to the ammonium phosphate processing stream in various proportions to yield products with various N:P ratios.

## EXPERIMENTAL

The gypsum-crystallizer filtrate was obtained from the TVA sulfate recycle process pilot plant (Meline *et al.*, 1971). The filtrate, including cake wash, typically contained (100% basis) about 24% ammonium nitrate, 8.5% phosphoric acid, 0.28% R<sub>2</sub>O<sub>3</sub>, and 3% ammonium sulfate. A typical analysis is shown in Table I.

In the initial work the filtrate was ammoniated in a single vessel equipped with an agitator and internal water cooling coils. Although large TAP crystals formed readily at pH 9 or above and 75° F, filtration rates were very low because of clogging of the filter medium by the precipitated impurities (Blouin *et al.*, 1970). Therefore tests were made of a two-stage ammoniation system similar to that developed by Houston *et al.* (1955) in pilot plant tests of producing diammonium phosphate from wet-process phosphoric acid.

Tennessee Valley Authority, Muscle Shoals, Alabama 35660

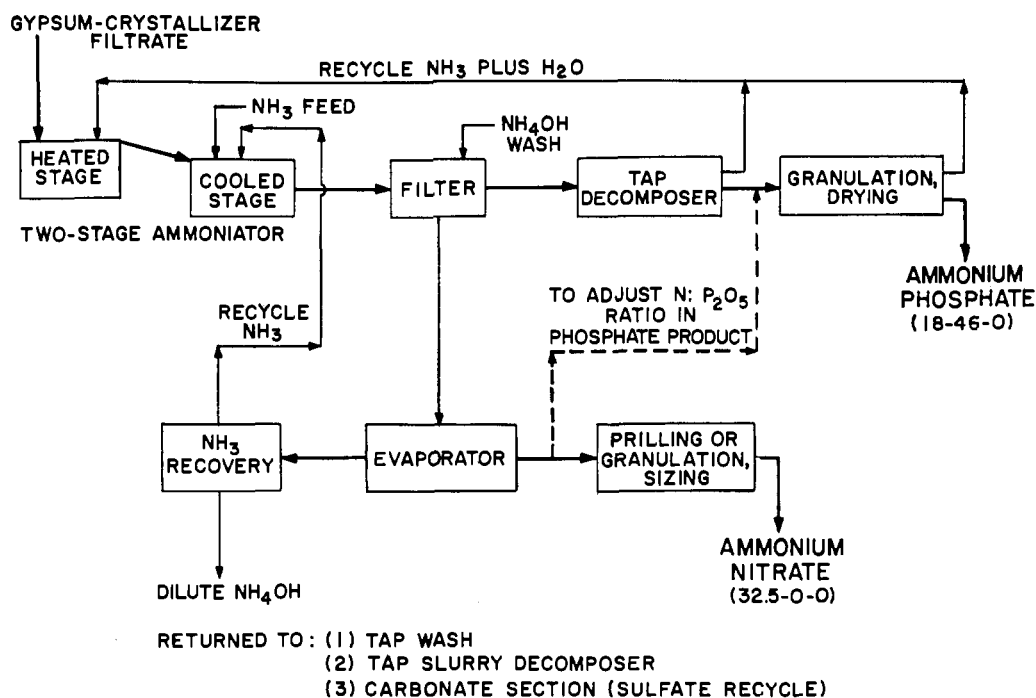


Figure 1. Separation of ammonium phosphate from ammonium nitrate in modified sulfate recycle nitric phosphate process

In that work ammoniation of the wet-process phosphoric acid to pH 5 at boiling resulted in agglomeration of the impurities to a readily filterable form before the pH was increased for precipitation of the diammonium phosphate.

In the present work in order to precipitate the phosphate as TAP, it was necessary to cool the slurry of precipitated impurities before continuation of ammoniation to the high pH desired. The development of optimum conditions for the process and the effects of variables in the first and second ammoniation stages are discussed below.

**First-Stage Ammoniation (Precipitation of Impurities).** A series of tests was made to determine the effects of pH, 4.0 to 5.7, temperature, 124° to 222° F, and retention time, 0.3 to 1.0 hr, on the filterability of impurities precipitated in the first stage. Preliminary tests had shown that the degree of filterability at this point would carry over to the second stage.

Gypsum-crystallizer filtrate was fed to the first stage at the rate of about 25 g/min; anhydrous ammonia was added in the ratio necessary to maintain the pH between 5.5 and 6.0. Because of heat losses from the small unit (4.5-in. diameter

Total	N		P	CaO	SO <sub>4</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	F
	NH <sub>3</sub>	NO <sub>2</sub>						
8.3	4.1	4.2	2.7	0.4	2.2	0.14	0.14	0.5

<sup>a</sup> Water used to wash gypsum cake added to filtrate.

× 8-in. high) and the low solution concentration, external heat was required to promote boiling (225–230° F). A low-speed agitator maintained the resulting agglomerates in suspension for overflow to the second stage. A feed rate of 25 g/min gave an average retention time of 1 hr in the first stage; lower retention times were obtained by decreasing the holdup in the vessel.

The slurry was filtered batchwise with a Buchner-type filter (10.1-in.<sup>2</sup> area) at a vacuum of 15 in. of Hg. Filtering rates are reported as dry agglomerated impurities, lb/(hr) (ft<sup>2</sup>). A fine polyethylene cloth that allowed no visible solids to pass was used. The results are given in Table II.

Table II. Effect of First-Stage Ammoniation Conditions on Filtering Rate of Agglomerates of Impurities from Gypsum-Crystallizer Filtrate<sup>a</sup>

Test no.	Ammoniation conditions			Composition of product solution, % NH <sub>4</sub> NO <sub>3</sub>	Filtering rate, lb dry cake/(hr) (ft <sup>2</sup> ) <sup>c</sup>	Impurities <sup>c</sup> precipitated, % of input
	Temperature, °F <sup>b</sup>	pH	Retention time, hr			
1	124	4.0	0.3	24.6	7	84.0 <sup>d</sup>
2	124	4.1	1.1	25.1	6	83.0 <sup>d</sup>
3	136	5.9	0.3	24.6	5	76.3 <sup>d</sup>
4	220	4.2	0.3	29.2	40	95.8 <sup>e</sup>
5	220	4.5	1.0	34.9	277	87.7 <sup>e</sup>
6	219	5.7	0.3	30.8	25	94.3 <sup>e</sup>
7	222	5.7	1.0	36.6	271	96.4 <sup>e</sup>

<sup>a</sup> Pilot-plant filtrate, analysis, %: total N, 8.3; NH<sub>3</sub>-N, 4.0; P<sub>2</sub>O<sub>5</sub>, 5.3; CaO, 0.50; SO<sub>4</sub>, 1.4; Fe<sub>2</sub>O<sub>3</sub>, 0.14; Al<sub>2</sub>O<sub>3</sub>, 0.15; and F, 0.5. <sup>b</sup> Low temperature was autogenous reaction temperature; higher temperature, boiling by external heat. <sup>c</sup> Iron, aluminum, and calcium phosphate. <sup>d</sup> Very fine particles. <sup>e</sup> Spherical agglomerates.

**Table III. Effect of Second-Stage pH on Filtering Rate and Phosphate Removal**

Test no. <sup>a</sup>	pH	Filtering rate, lb/(hr) (ft <sup>2</sup> ) <sup>b,c</sup>	Phosphate removal, %
1	9.0	125	74
2	9.2	180	88
3	9.4	250	96
4	9.6	400	99
5	9.8	725	99
6	10.0	1575	99

<sup>a</sup> Feed concentration, 36% ammonium nitrate. <sup>b</sup> Cake thickness, 2 in. <sup>c</sup> Basis: dry, stabilized ammonium phosphate.

**Table IV. Effect of Feed Concentration<sup>a</sup> to the Second Stage on Filtering Rate and Separation of Phosphate**

Test no.	Feed concentration, wt% NH <sub>4</sub> NO <sub>3</sub> <sup>a</sup>	Cake thickness, in.	Filtering rate, lb/(hr) (ft <sup>2</sup> ) <sup>b</sup>	Phosphate removal, %
1	33.7	1.9	984	98.4
2	36.6	2.3	1785	99.5
3	40.0	2.4	1098	99.5

<sup>a</sup> Concentration based on liquid phase (solids free) of first stage. <sup>b</sup> Basis: dry, stabilized ammonium phosphate.

**Table V. Effect of Second-Stage Temperature on Filtering Rate and Separation of Phosphate**

Test no.	Second-stage conditions <sup>a</sup>		Cake thickness, in.	Filtering rate, lb/(hr) (ft <sup>2</sup> ) <sup>b</sup>	Phosphate removal, %
	Temperature, °F	pH			
1	50	10.0	2.3	1125	99.0
2	70	10.0	2.2	1860	99.0
3	90	9.9	2.5	2210	99.0
4	110	9.3	2.3	2710	97.6
5	130	9.0	1.5	1600	90.5

<sup>a</sup> Feed concentration to second stage, 39.8% ammonium nitrate. <sup>b</sup> Basis: dry, stabilized ammonium phosphate.

At autogenous temperatures of 124° to 136° F and with pH of 4.0 to 5.9, very poor filtration rates were obtained—less than 10 lb/(hr) (ft<sup>2</sup>)—and there was no benefit with increased retention time. The solids were extremely fine and blinded the filter cloth. When the temperature during ammoniation was increased to about 220° F, spherical agglomerates averaging about 30 μ in size were formed. Filtration rate improved significantly with increase in retention time, reaching 275 lb/(hr) (ft<sup>2</sup>) at a time of 1 hr. Varying the pH did not affect filtration, and the effect on degree of impurity precipitation was inconclusive; however, since it was desirable to obtain as much heat of reaction as possible in the first stage, the higher pH level was later used. In subsequent tests involving crystallization and filtration of TAP, conditions in the first stage were: temperature, 220° to 230° F (boiling by addition of heat); pH, 5.5 to 6.0; and retention time, 1 hr.

**Second-Stage Ammoniation (Crystallization of TAP).** No serious difficulties were encountered in filtering the slurry from the second stage, provided the impurities were pre-

cipitated as agglomerates described above. However, all of the variables in the second stage—pH, feed concentration, temperature, and TAP cake-washing conditions—had significant effects on the filtration rates and degree of separation of the ammonium phosphate and ammonium nitrate.

The second-stage reactor (4.5-in. diameter × 8-in. high) was equipped with internal water coils for cooling and with a low speed agitator to prevent settling of solids. The pH in this stage was monitored continuously. The slurry from the first stage overflowed to the second stage. Filtering of product was carried out as described previously for the first stage. The filtration rate was expressed as pounds of dry stabilized ammonium phosphate cake per hour per square foot of filter cloth. As indicated previously, stabilization of the TAP was accomplished by heating to drive off about 1 mol of NH<sub>3</sub> per mol of TAP.

**EFFECT OF pH.** The second-stage pH was varied from 9 to 10 while the temperature was held at 75° F by cooling. Feed to this stage was a thin slurry of agglomerates formed in the first stage. The feed concentration was constant at 36% ammonium nitrate—fixed by first-stage conditions: temperature, 225° F; pH, 5.7; and retention time, 1 hr. Results are given in Table III.

Increasing the pH from 9 to 10 resulted in an increase in the filtering rate of the TAP slurry from about 125 to 1600 lb/(hr) (ft<sup>2</sup>). Phosphate removal increased from 75 to 99%. The average TAP crystal size was 200 by 300 μ. A minor phase of needle crystals (10 × 150 μ) believed to be complexes of 3NH<sub>4</sub>NO<sub>3</sub>·1(NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub> or 2(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>·1(NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub> (Flatt *et al.*, 1955) was also observed.

From the results of these tests it was concluded that subsequent tests should be made at a pH of 9.8 to 10. However, in some tests made at high temperatures (above 100° F) and atmospheric pressure, a pH higher than 9.3 could not be attained because the partial pressure of ammonia was too high.

**EFFECT OF FEED CONCENTRATION.** Operation of the first stage at boiling for 1 hr resulted in a slurry containing 36% ammonium nitrate. Since water must be removed at some point in the system to obtain solid products, it would be desirable to remove as much in the first stage as possible while maintaining a filterable slurry. This would save on volume of slurry to be handled in subsequent steps. Therefore, tests were made with feed to the second stage containing 33, 36, and 40% ammonium nitrate. The pH was held at 9.9 in all tests. The data of Table IV show that the filtering rates were satisfactorily high [980–1785 lb/(hr) (ft<sup>2</sup>)] with feed concentrations in this range. Phosphate removal was 98.4 to 99.5%. The 40% feed concentration resulted in a fairly viscous slurry after ammoniation and probably is the highest concentration that could be used.

At 33% ammonium nitrate, only TAP crystals of about 50 × 110 μ and agglomerates of about 30 μ average size were present in the cake. At the higher concentrations, some of the complexes mentioned earlier were formed. These complexes were not observed in the washed TAP filter cakes.

**EFFECT OF TEMPERATURE.** Cooling in the second stage is required, but lower cooling water requirements could be achieved by operating the second stage at as high a temperature as possible. Tests were made in which the second-stage temperature was varied from 50° to 130° F by varying the amount of cooling water used; the autogenous temperature (no cooling) in the bench-scale equipment was 130° F. The data are given in Table V.

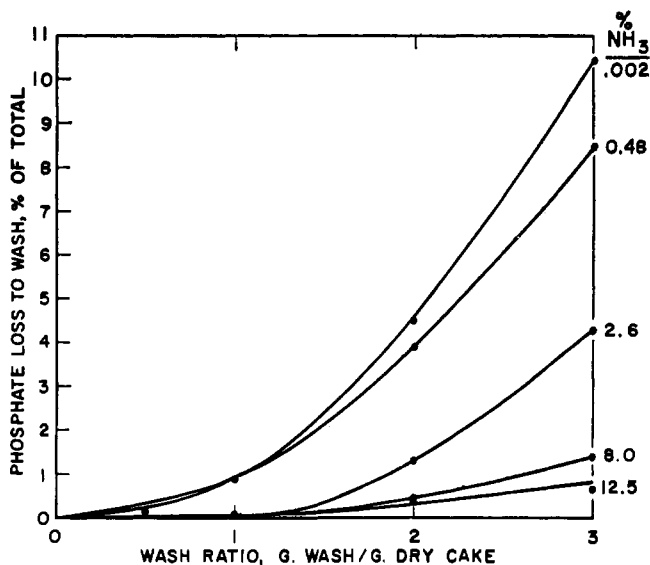


Figure 2. Effects of TAP cake wash ratio and concentration on phosphate loss

The filtering rate increased from 1100 to 2700 lb/(hr) (ft<sup>2</sup>) with increase in temperature from 50° to 110° F and decreased sharply at 130° F. Another disadvantage of temperature above 110° F at atmospheric pressure is that the vapor pressure of the ammonia was unacceptably high and phosphate removal decreased. Phosphate removal of 98 to 99% was obtained in the range of 50° to 110° F, but decreased to only 91% at 130° F. It was concluded that the highest second-stage temperature for an acceptable degree of phosphate removal was 110° F.

**Washing TAP Cake.** On a dry stabilized basis, the unwashed cake from the second-stage ammoniation contained about 7% nitrate nitrogen when the feed to the second stage contained 36% ammonium nitrate, and the second stage was at a temperature of about 100° F. This nitrate nitrogen could be removed from the wet cake by washing with ammonium hydroxide solution.

The concentration of ammonia in the wash solution had no effect on nitrate removal but did affect phosphate loss to the wash filtrate. The data of Table VI show that when the ratio of wash solution to cake was increased from 0 to 2 g/g dry cake equivalent, the nitrate nitrogen content of the cake decreased from 7.2 to 1.1%. Further increase to 3 g wash in these single-stage washing tests was of no significant benefit in removing nitrate but resulted in some further removal of sulfate, as indicated by the somewhat greater

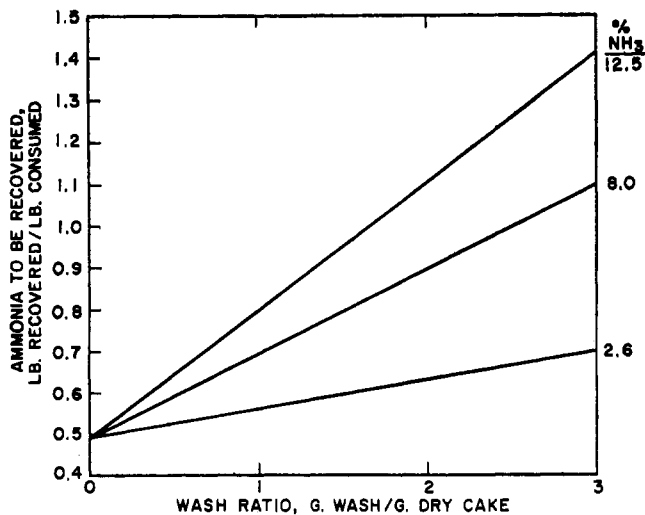


Figure 3. Effects of wash ratio and concentration on ammonia recovery requirement

total nutrient content of the product after washing at the higher rate. The compositions of the stabilized ammonium phosphates from washing at the rate of 2 and 3 g/g cake, dry basis, were 18.8-19.3-0 and 18.5-20.3-0 N-P-K (18.8-44.2-0 and 18.5-46.5-0 N-P<sub>2</sub>O<sub>5</sub>-K<sub>2</sub>O), respectively.

The data plotted in Figure 2 show that phosphate loss or removal from the cake was 1% or less when the wash solution contained at least 2.5% ammonia with a wash ratio of 2. With a wash ratio of 3, an ammonia concentration of about 8% was needed to limit phosphate loss to 1%.

Water added as wash solution must be removed from the system by evaporation; the use of a wash ratio of 2 added about 40% to the evaporation load.

**Ammonia Recovery.** Ammonia must be recovered from two steps in the process: (1) the decomposition of TAP cake to form a stable phosphate such as diammonium phosphate and (2) the ammonium nitrate solution (dissolved free NH<sub>3</sub>) during concentration to a solid. In large-scale operation, the ammonia from decomposition of the TAP would be recycled, along with water vapor, directly to the first-stage ammoniator, where evaporation of any excess water would be controlled to give the desired ammonium nitrate concentration. Part of the ammonia evolved during concentration of the filtrate (ammonium nitrate solution) would be recycled to the second-stage (TAP) crystallizer, and the remainder would be recycled to the TAP cake wash and to the gypsum-conversion unit in the basic sulfate recycle process.

Figure 3 shows the effect of TAP wash conditions on the

Table VI. Effect of Wash Ratio on Removal of Nitrate Nitrogen from Filter Cake

Test no.	Wash ratio, g wash liquor <sup>a</sup> /g dry stable cake <sup>b</sup>	Cake analysis, <sup>b</sup> wt% (dry)					
		Total	NH <sub>3</sub>	NO <sub>3</sub>	P	(P <sub>2</sub> O <sub>5</sub> )	SO <sub>3</sub>
1	0	25.3	18.1	7.2	11.2	(25.6)	3.5
2	0.5	24.0	17.9	6.1	12.9	(29.5)	
3	1	22.4	17.9	4.5	15.3	(35.0)	
4	2	18.8	17.7	1.1	19.3	(44.2)	
5	3	18.5	17.4	1.1	20.3	(46.5)	

<sup>a</sup> Wash liquor was 2.6% NH<sub>3</sub> solution. <sup>b</sup> Product from decomposition of TAP filter cake.

quantity of excess ammonia that must be recovered and recycled over that consumed by the formation of ammonium phosphate and ammonium nitrate in the basic sulfate recycle process. When the ratio of wash to dry cake ratio is 2 and the concentration of ammonia in the wash solution is 2.6%, the amount of ammonia to be recycled would be 0.63 lb/lb fixed as product. With a wash ratio of 3 and a wash concentration of 8% ammonia (to prevent excessive loss of phosphate), the amount of ammonia to be recycled is 1.1 lb/lb ammonia fixed. It is suggested that more efficient cake washing, which may be obtained in countercurrent operation, would reduce the amount to be recycled.

#### LITERATURE CITED

- Blouin, G. M., Livingston, O. W., Getsinger, J. G., *J. Agr. Food Chem.* **18**, 313 (1970).  
Flatt, R., Brunisholz, G., Rod, P., *Helv. Chim. Acta* **38**, 769 (1955).  
Houston, E. C., Yates, L. D., Haunschild, R. L., *J. Agr. Food Chem.* **3**, 43 (1955).  
McFarlin, R. F., Brown, W. E., *Proc. Fert. Ind. Round Table 1968* 108 (1968).  
Meline, R. S., Faucett, H. L., Davis, C. H., Shirley, A. R., Jr., *Ind. Eng. Chem. Process Des. Develop.* **10**, 257 (1971).  
Strelzoff, S., Dell, G., *Proc. Fert. Ind. Round Table 1968* 90 (1968).  
Strelzoff, S., Roberts, E. S., U. S. Patent 2,689,175 (September 14, 1954).

*Received for review February 8, 1971. Accepted March 18, 1971. Presented at Division of Fertilizer and Soil Chemistry, 160th National Meeting, ACS, Chicago, Illinois, September 13-18, 1970.*