NITRIC PHOSPHATES

Manufacture from Phosphate Rock, Nitric Acid, Ammonia, and Potassium or Other Soluble Sulfates

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A fertilizer production process has been developed on a pilot plant scale, which is not dependent on sulfuric acid. Phosphate rock was acidulated with nitric acid, potassium or another soluble sulfate was added, and the resultant slurry was ammoniated, dried, and granulated. With potassium sulfate, the grade of a typical product was 12–12–12; with ammonium sulfate, the grade was 17–13–0. The calcium content of the rock, which formed calcium nitrate during acidulation, was converted to calcium sulfate and dicalcium phosphate. The soluble sulfate added was sufficient to avoid presence of calcium nitrate in the final product, undesirable because of hygroscopicity. Promising results were obtained in small scale tests in which langbeinite or glaserite provided the sulfate and potassium chloride was added to increase the K_2O/P_2O_5 weight ratio to 1. The grades of these products were 10–10–10 and 11–11–11. The products contained 96% or more of their phosphorus pentoxide in citrate-soluble form, and 5 to 11% was water-soluble. Favorable results were obtained in greenhouse tests of products made with potassium sulfate and ammonium sulfate. Physical properties of these products and of products made with langbeinite and glaserite are satisfactory. Estimates indicate that the process is economically attractive.

PRODUCTION OF NITRIC-PHOSPHATE FERTILIZERS has been described (4, 5, 11), in which mixtures of nitric and phosphoric or sulfuric acids are used in the acidulation of phosphate rock. The chief reason for using phosphoric or sulfuric acid is to prevent the presence of calcium nitrate in the product and thereby eliminate excessive hygroscopicity.

The present paper describes the development of a nitric-phosphate process in which nitric acid is the only acid used. Elimination of calcium nitrate from the product and the production of a three-component (N-P$_2$O$_5$-K$_2$O) fertilizer are achieved through the use of potassium sulfate. From the viewpoint of conserving this country's reserve of elemental sulfur, this process is of consider-

able interest because potassium sulfate is made from langbeinite (3), an ore that contains potassium and magnesium sulfates. Reserves of langbeinite are known to be extensive.

In the initial work by TVA on the nitric acid fertilizer processes, studies were made of the feasibility of producing nitrogen-phosphate fertilizers by methods that involved acidulating phosphate rock with nitric acid alone and then drying the product at 180° F. (6–9) or drying at about 300° F. in a closed system to evolve a large portion of the nitric acid, which was recovered (12, 13). Neither method gave promising results. Drying of the acidulates at 180° F. resulted in a very hygroscopic product and excessive loss of nitrogen. Loss of nitrogen dur-

ing drying was found to be caused by the continuing reaction between the mono-calcium phosphate and calcium nitrate present in the acidulate as indicated in Equation 1.

$$Ca(H_2PO_4)_2 + Ca(NO_3)_2 \rightarrow 2CaHPO_4 + 2HNO_3 \quad (1)$$
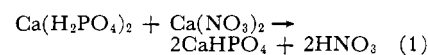
Heating at 300° F. to drive off nitric acid gave a hygroscopic product in which the availability of the phosphorus pentoxide was only about 86%. No significant improvement in the physical properties of the products from acidulation of phosphate rock with nitric acid was achieved through the use of conditioners. Treating the acidulate with anhydrous ammonia to precipitate most of the phosphate in the form of dicalcium phos-

Table I. Typical Chemical and Screen Analyses of Raw Materials Used in Pilot Plant Tests

| Material | Composition, % | | | | | | | | | | | | | | Screen Analysis, % of Size Fraction Indicated (U. S. Series No.) | | | | |
	P_2O_5	CaO	F	CO_2	Fe_2O_3	Al_2O_3	Acid-insoluble	Ignition loss	H_2O	K_2O^a	SO_3	Cl	MgO	N	+35	-35 +60	-60 +80	-80 +100	-100
Phosphate rock[b]	34.2	48.0	3.9	2.6	0.9	0.7	3.4	4.0	1.0	..	..	..	..	..	0.3	40.7	22.4	17.1	19.5
K_2SO_4, domestic[c]	..	0.6	..	..	..	..	..	..	0.2	49.7	44.7	1.6	1.3	..	13.3	20.9	15.1	12.8	37.9
K_2SO_4, imported[d]	..	1.0	..	..	..	..	..	..	1.1	49.0	44.7	1.0	1.4	..	7.9	14.6	35.1	18.9	23.5
$(NH_4)_2SO_4$	..	..	..	..	..	..	..	..	0.2	..	60.0	..	..	20.9	4.8	55.4	22.4	15.3	2.1

[a] Soluble in ammonium oxalate as defined by AOAC (1).
[b] Screened Florida flotation concentrate, +35-mesh fraction added after grinding.
[c] Made from langbeinite.
[d] Made from potassium chloride and sulfuric acid.

phate and convert some of the calcium nitrate to ammonium nitrate minimized loss of nitrogen during drying. Although ammoniation decreased the calcium nitrate content of the product from 45 to 23%, the ammoniated product was only somewhat less hygroscopic. Addition of potassium sulfate to react with the calcium nitrate present after ammoniation resulted in a product with satisfactory physical properties.

The process involving the use of potassium sulfate first was studied in small scale equipment and then was tested in the pilot plant that had been used in the development of the other nitric-phosphate processes (5, 11). Only a few minor modifications to the pilot plant were required.

In the pilot plant work, phosphate rock and nitric acid were mixed in proportions such that the HNO_3/CaO mole ratio was about 1.8. The principal products of the acidulation reaction were believed to be phosphoric acid, monocalcium phosphate, calcium nitrate, and hydrogen fluoride. Ammonia was added to convert the monocalcium phosphate and the phosphoric acid to dicalcium phosphate. A part of the calcium nitrate entered into the reaction, the calcium going to form the dicalcium phosphate and some calcium fluoride and the nitrate going to form ammonium nitrate. Potassium sulfate was added to convert the remaining calcium nitrate to calcium sulfate and potassium nitrate. Part of the potassium sulfate was added during the initial stage of ammoniation and the remainder between the two drying steps. About 15% more potassium sulfate than that required to eliminate the calcium nitrate usually was added to obtain a product in which the P_2O_5/K_2O weight ratio was 1. An acidulation mole ratio (HNO_3/CaO) of 1.8 was used because, in the small scale tests, it had resulted in a product in which essentially all the phosphorus pentoxide was available (citrate-soluble).

The effect of degree of acidulation on availability of phosphorus pentoxide in products of the small scale tests is shown

in Figure 1. In these tests, carried out with potassium sulfate added prior to ammoniation, the degree of ammoniation was such as to precipitate substantially all the phosphorus pentoxide as dicalcium phosphate and the fluorine as calcium fluoride.

Acidulation

Florida phosphate rock (flotation concentrate) ground to pass a 35-mesh screen was used in most of the pilot plant work. Typical chemical and screen analyses of the ground phosphate are shown in Table I. The nitric acid was available from TVA operations and varied in concentration from 39 to 42%. The phosphate was delivered to the acidulation train at a rate of 150 pounds per hour by a screw feeder attached to the bottom of a hopper that rested on platform scales. The nitric acid was pumped through a rotameter from storage tanks at a rate of about 36 gallons per hour. The degree of acidulation, HNO_3/CaO mole ratio, averaged 1.8.

Continuous acidulation was carried out in the equipment described for the other nitric acid processes (5, 11), except that, in most of the work, three acidulation tanks were used to give a retention time of 40 minutes. Later tests, however, showed that two tanks, which gave a retention time of 30 minutes, were adequate and that 20-mesh material was sufficiently fine.

The tanks, two of which were made of AISI Type 304 stainless steel and the other of AISI Type 316 stainless steel, were 3.5 feet high and 1 foot in diameter. Each tank was equipped with a motor-driven propeller-type agitator; a foam breaker was attached to the agitator shaft. The slurry level allowed 45% freeboard for foaming; the tests indicated, however, that 20% freeboard was sufficient in all but the first extractor.
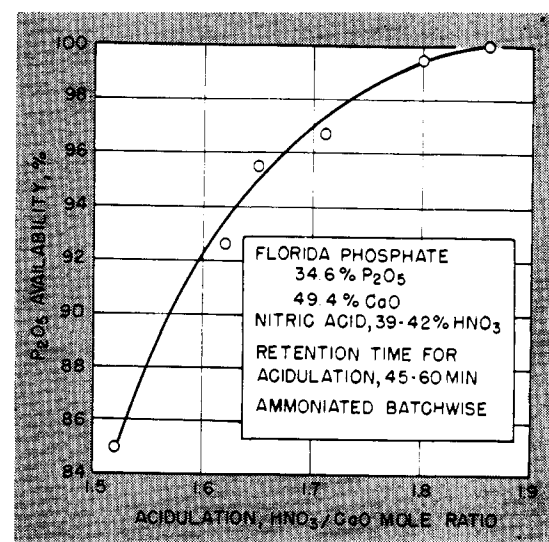
The phosphate rock and acid were fed at room temperature, and the heat of the reaction raised the temperature of the acidulate to about 145° F. The specific gravity of the acidulate at this tempera-

ture was about 1.47. Loss of nitrogen during the acidulation step was about 1%, and about 10% of the fluorine in the phosphate rock was evolved. The acidulate, which contained about 43% water, flowed to the ammoniation train by gravity at a rate of about 42 gallons per hour.

Ammoniation and Potassium Sulfate Addition

Small scale studies of the ammoniation step of the process, without addition of potassium sulfate, were made with the results shown in Table II. In these tests the ammoniation was carried out batchwise, which had been found to be the best method of maintaining high phosphorus pentoxide availability. The extraction slurry had been prepared by acidulating phosphate rock with nitric acid in proportions to give a HNO_3/CaO mole ratio of 1.86. With this acidulation and with the rock of the composition that was used in these tests, the amount of ammonia stoichiometrically required to precipitate all the phosphorus pent-

Figure 1. Effect of degree of acidulation on availability of P_2O_5 in product

FLORIDA PHOSPHATE
34.6 % P_2O_5
49.4 % CaO
NITRIC ACID, 39-42% HNO_3
RETENTION TIME FOR ACIDULATION, 45-60 MIN
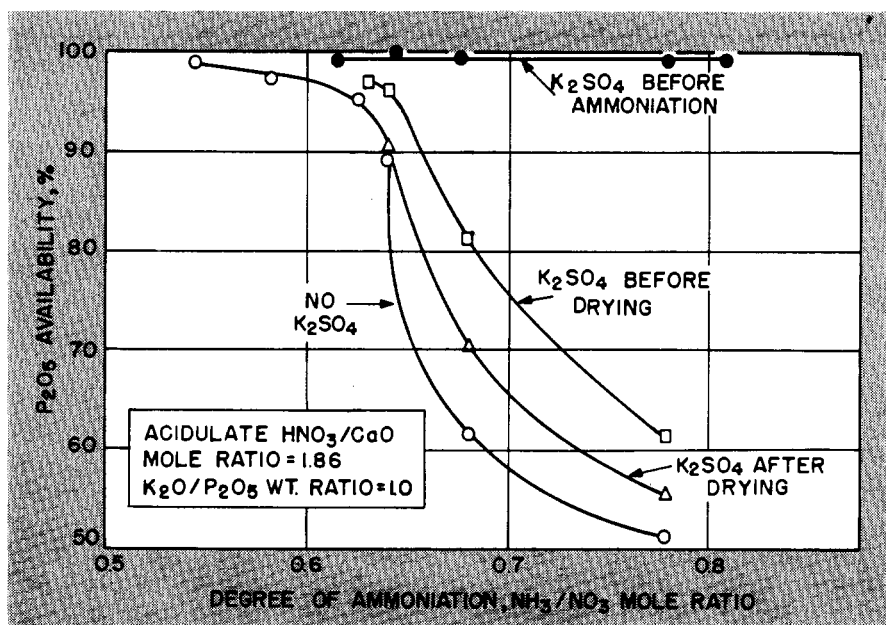AMMONIATED BATCHWISE

Figure 2. Effect of point of addition of potassium sulfate on availability of P_2O_5 in product

oxide as dicalcium phosphate was equivalent to a mole ratio of $NH_3/NO_3 = 0.63$. There was an appreciable loss of phosphorus pentoxide availability when the NH_3/NO_3 ratio approached 0.63 and serious loss when the ratio slightly exceeded 0.63, as shown in Table II.

However, there was no loss of phosphorus pentoxide availability when potassium sulfate was present in the slurry during ammoniation. Figure 2 shows the effect of potassium sulfate on phosphorus pentoxide availability in the product. In these tests sufficient potassium sulfate was added to give a product in which the K_2O/P_2O_5 weight ratio was 1. When the sulfate was added after drying or after ammoniation but before drying, there was only a slight improvement in phosphorus pentoxide availability and the degree of ammoniation could be carried only a little above 0.63 before serious loss occurred. When the sulfate was added before ammoniation, no loss in phosphorus pentoxide availability occurred even though the degree of ammoniation was carried to an NH_3/NO_3 mole ratio of 0.81. The presence of sulfate, therefore, eliminated the need for very careful control of the ammoniation step of the process. Even when the NH_3/NO_3 mole ratio was as high as 0.81, there was no loss of ammonia from the slurry.

In later work it was found that the quantity of potassium sulfate required to prevent loss of phosphorus pentoxide availability during ammoniation was only about 15% of that required for a K_2O/P_2O_5 weight ratio of 1. In the small scale tests of continuous ammoniation, excessive gelling occurred when more than three fourths of the potassium sulfate required for a K_2O/P_2O_5 weight ratio of 1 was added in the first ammoniator. Consequently, most of the pilot plant tests were made with 60 to 80% of the sulfate added in the first ammoniator and the remainder added to the partially dried ammoniated slurry. No gelling occurred in the pilot plant even when the potassium sulfate was added in the first ammoniator in proportions such that the K_2O/P_2O_5 weight ratio was 0.8. The slurries were so fluid that it appeared that all the potassium sulfate could have been added in the first ammoniator without difficulty.

About the time that the small scale tests were completed, a British patent (10) was issued to Potasse et Engrais Chimiques on the use of potassium sulfate in a nitric acid process. The patent states that potassium sulfate cannot be added with the nitric acid during decomposition of phosphate rock because the formation of aqua regia from the chlorides present in commercial potassium sulfate would increase the corrosion of equipment. The patent claims the addition of potassium sulfate after ammoniation and cites as an example that mixing of the sulfate required 30 minutes and that the resultant thick paste was

dried in a tray dryer. The method evolved by TVA—that is, the addition of potassium sulfate during ammoniation—does not increase corrosion of equipment, eliminates a separate mixing step, and has the additional advantage of obviating the need for close control during ammoniation.

The ammoniation train was the one described by Striplin and coworkers in their work on the nitric-sulfuric acid process (11). It consisted of four stainless steel tanks, each 4 feet high and 2 feet in diameter. Each tank was provided with two turbo-impellers, one 12 inches and one 10 inches in diameter, which were mounted on the same shaft and were rotated at 200 r.p.m. by a 3.5-hp. motor. The freeboard in each tank was 50%, although in this process 25% of freeboard was found to be sufficient.

Ammonia gas, supplied at 20 pounds per square inch, was measured with rotameters and added to each ammoniator through a $1/_2$-inch pipe extending below and near the lower impeller. The ammonia feed rate was 25 pounds per hour, and the NH_3/NO_3 mole ratio averaged about 0.6. About 60% of the ammonia was added in the first ammoniator, 20% in the second, 15% in the third, and 5% in the fourth. This stepwise decrease in addition of ammonia was used because earlier small scale tests without potassium sulfate had shown that the rate of addition of ammonia had to be decreased as ammoniation approached completion in order to avoid loss of phosphorus pentoxide availability. The effect of rate of ammoniation on phosphorus pentoxide availability in slurries containing potassium sulfate was not studied.

The temperature of the slurry during ammoniation rose to 180° F. in the first stage and dropped gradually in the remaining stages to 170° F. The slurry discharged from the fourth ammoniator averaged 32 to 36% water as compared with the 43% water content of the acidulate. About 14% of the original water was evaporated during ammoniation. There was no loss of ammonia during ammoniation.

Table II. Effect of Degree of Ammoniation on Phosphorus Pentoxide Availability[a]

Degree of ammoniation, NH_3/NO_3 mole ratio[b]	0.46	0.52	0.57	0.61	0.66	0.73	0.80
Chemical analysis of dried product[c], %							
Total P_2O_5	16.3	16.2	16.8	15.2	15.4	15.8	15.2
Citrate-insoluble P_2O_5	0.2	0.1	0.4	0.7	2.4	6.1	7.6
Total N	14.9	15.3	15.5	16.2	16.3	16.9	17.9
NO_3 nitrogen	10.2	9.9	9.8	10.0	9.9	9.7	9.8
NH_3 nitrogen	4.7	5.4	5.7	6.2	6.4	7.2	8.1
P_2O_5 availability, %	98.9	99.4	97.7	95.5	84.5	61.5	50.0

[a] Florida phosphate rock (32.4% P_2O_5, 47.0% CaO) and 42% HNO_3 used. Acidulation mole ratio $HNO_3/CaO = 1.86$.
[b] Ammoniation rate, 0.009 lb. $NH_3/(min.)(lb. slurry)$. Degree of ammoniation from analysis of slurry.
[c] Dried in tray dryer at 180° F. for 24 hours.

From 60 to 80% of the total amount of potassium sulfate used was added in the first ammoniator; the remainder was added to the fluid discharge from the first-stage dryer. The total amount of potassium sulfate, about 100 pounds per hour, was that necessary to give a K_2O/P_2O_5 weight ratio of 1 and was about 15% more than that needed to convert the calcium nitrate present after ammoniation to calcium sulfate. A disk-type volumetric feeder was used to add the potassium sulfate continuously to the first ammoniator. The agitation in the ammoniator was sufficient to disperse the sulfate into the slurry, and there was no formation of lumps. Most of the tests were made using imported potassium sulfate because domestic potassium sulfate was not available at the time the tests were made. As shown in Table I, the compositions of potassium sulfate from both sources were essentially the same. All sulfate was passed through a 20-mesh screen to remove lumps and trash.

Drying

A two-stage drying procedure was used. This procedure consisted of the following steps:

1. Partially drying the ammoniated slurry (32 to 36% water), which contained 60 to 80% of the total potassium sulfate required to obtain a P_2O_5/K_2O weight ratio of 1, to a water content of about 12% in a rotary dryer operated with inlet gas at 1500° to 1600° F. and exit gas at 500° F.; the temperature of the material discharged from this dryer averaged about 230° F.
2. Mixing the partially dried fluid material with recycled dried product and the remainder of the potassium sulfate in a double-shaft paddle mixer.
3. Drying the mixture, which contained about 4% water, in a rotary dryer operated with inlet gas at 450° F. and exit gas at 200° F.; the temperature of the product from this dryer averaged about 190° F.
4. Cooling, screening, and bagging the product.

The product (−6 +50 mesh) contained 1 to 2% moisture. The first-stage dryer had a greater capacity than the other parts of the pilot plant and was operated discontinuously 70% of the time.

The first-stage dryer, which in effect was a rotary evaporator, was operated with cocurrent feed and drying gas, was 1.5 feet in diameter and 10 feet long, and contained eight stainless steel radial flights. It was operated at 18 to 20 r.p.m. with a slope of 0.2 inch per foot; the feed rate was about 1000 pounds (80 gallons) of slurry per hour. The flights were 4 inches wide from the discharge end to the center of the dryer and then tapered to 1 inch at the inlet. A retaining ring at the inlet of the dryer and a truncated cone at the discharge end

maintained a pool of slurry in the dryer so that the flights raised the slurry and dropped it as a series of curtains parallel to the axis of the dryer. When this dryer was operated with inlet gas at 1700° F., the water content of the product, which was fluid, was 10 to 12%, and the loss of nitrogen was less than 1% of the nitrogen input. The retention time of material in this dryer was about 30 minutes.

The chief purpose of the paddle mixer was for mixing recycled dry product with the partially dried slurry from the first-stage dryer to obtain a granular material, containing about 4% moisture, that could be dried further without difficulty. The final addition of potassium sulfate also was made at this point to obtain homogeneous incorporation. The total retention time of the slurry in the mixer was about 3 minutes; about half of this time was allowed for incorporation of potassium sulfate and the other half for the addition of recycled product and for granulation. A ratio of 2 to 1 of recycled dry product to partially dried

slurry was required to obtain a satisfactory feed for the second-stage dryer.

Second-stage drying was carried out in a Roto-Louvre dryer (Link Belt catalog No. 207–10), which usually was operated at a feed rate of 1500 pounds per hour with an inlet gas temperature of 450° F. and an outlet gas temperature of 200° to 210° F.; the ratio of drying gas to feed (pounds of air per pound of feed) was about 1.7. Under these conditions the product, which contained 1 to 2% moisture, was discharged at a temperature of 175° to 195° F. and loss of nitrogen during drying was negligible. About 40% of the product was in the form of −6 +50-mesh granules. The amount of oversize and undersize, separated by screening, was about equal to that required for recycling to the paddle mixer.

Typical Operating Data

A summary of data collected during two typical pilot plant tests is given in Table III (tests 1 and 2); analyses of the products are given in Table IV.

Table III. Summary of Operating Data

	Test No.		
	1	2	3
Acidulation			
Phosphate rock			
Feed rate, lb./hour	150	150	150
P_2O_5 content, %	34.9	34.7	34.9
CaO content, %	50.1	48.6	48.6
Nitric acid			
Feed rate, lb./hour	380	384	382
HNO_3 content, %	39.6	39.5	39.7
Ammoniation			
Potassium sulfate feed rate[a], lb./hour	64	64	..
Ammonium sulfate feed rate[a], lb./hour	..	..	76
Ammonia rate, lb./hour			
First stage	14.8	14.7	14.4
Second stage	4.6	5.4	7.4
Third stage	3.4	3.2	2.5
Fourth stage	1.4	1.2	1.0
Ammoniated slurry output			
Rate, lb./hour	580	585	595
pH	3.0	2.7	3.5
P_2O_5 availability, %	97.7	98.0	97.2
First-stage drying			
Slurry feed rate, lb./hour	1152	885	1095
Inlet gas temperature, ° F.	1495	1550	1507
Exit gas temperature, ° F.	398	415	422
Product temperature, ° F.	222	228	243
Moisture content of feed, %	31.8	36.0	32.8
Moisture content of product, %	11.2	12.7	7.7
Nitrogen loss[b], %	0	1.4	2.1
Paddle mixer operation			
Concentrated slurry from first-stage dryer, lb./hour	875	650	800
Potassium sulfate feed rate, lb./hour	86	61	..
Recycled dried product feed rate, lb./hour	1840	1230	1200
Output, lb./hour	2801	1941	2000
Second-stage drying			
Input from paddle mixer, lb./hour	1700	1500	1338
Inlet gas temperature, ° F.	442	458	308
Exit gas temperature, ° F.	198	213	194
Product temperature, ° F.	174	194	175
Moisture content of feed, %	3.9	4.4	3.3
Moisture content of product, %	1.5	2.5	1.7
Nitrogen loss, %	0	0	1.3

[a] Added to first ammoniation stage.
[b] N loss through acidulation, ammoniation, and first-stage drying.

Table IV. Chemical Analyses[a] of Bagged Product Made from Phosphate Rock, Nitric Acid, Ammonia, and Potassium or Ammonium Sulfate

| Test No. | Nitrogen, % | | | P_2O_5, % | | | | K_2O, % | H_2O, % | SO_3, % | CaO % |
	Total	NH_3	NO_3	Total	Citrate-insoluble	Water-soluble	Avail-ability				
1[b]	12.2	4.7	7.5	12.1	0.4	1.0	96.7	12.9	1.0	11.6	17.2
2[b]	12.4	4.6	7.8	12.2	0.4	0.5	96.7	11.9	1.4	10.8	17.1
3[c]	17.3	8.9	8.4	13.4	0.5	1.5	96.0	..	1.0	10.9	18.8

[a] Analyses performed according to methods of AOAC (7).
[b] Made with potassium sulfate.
[c] Made with ammonium sulfate.

Each test was 1 week long. The plant was operated as a continuous, integrated unit except for the drying section, which was operated intermittently. No difficulties were encountered in operation of the pilot plant. The acidulation HNO_3/ CaO mole ratio varied from 1.62 to 1.95 and the degree of ammoniation varied from 0.59 to 0.68 NH_3/NO_3 mole ratio. The availability of the phosphorus pentoxide in the ammoniated slurry averaged about 98%. The availability of the phosphorus pentoxide in the final product was 96.7%. The rate of production was about 4 tons of finished product (−6 +50 mesh) per day. Analyses of the products indicated a loss of 1.4% of the total nitrogen used, a loss of 3.3% of the phosphorus pentoxide as citrate-insoluble phosphorus pentoxide, and no loss of potassium oxide as indicated by the AOAC method of analysis for fertilizers (7). About 3% of the discharge from the second-stage dryer was recovered as dust in a cyclone and returned to the process as recycle to the paddle mixer.

The total amount of heat required for drying the ammoniated slurry to a final moisture content of 1 to 2% was 2,300,-000 B.t.u. per ton of final product. Of this heat, 60% was required in the first drying stage and 40% in the second stage.

Cost estimates indicated the process to be economically attractive.

Tests with Ammonium Sulfate, Langbeinite, and Glaserite

The pilot plant was operated without difficulty for 1 week using ammonium sulfate instead of potassium sulfate to produce a nitric phosphate containing 17% nitrogen and 13% phosphorus pentoxide. Ammonium sulfate is produced as a by-product from coke oven operations. It can be produced without the use of sulfuric acid from gypsum, carbon dioxide, and ammonia (2).

The conditions for acidulation, ammoniation, and drying were the same as those used with potassium sulfate, except that all the ammonium sulfate required to convert the calcium nitrate to calcium sulfate was added to the first ammoniator.

Crystalline commercial ammonium sulfate was used in this test (Table I) instead of a 37% solution of ammonium sulfate, such as would be available in the

gypsum process prior to the crystallization step. The use of crystalline ammonium sulfate probably affected only the heat requirements of the first drying step. The product from the first-stage dryer (rotary) was a hot fluid melt that contained 8 to 10% moisture. This hot melt was mixed with previously dried material in the paddle mixer, and the discharge from the mixer was dried in the second-stage (Roto-Louvre) dryer. Test data and chemical analyses of the material at various stages in the process are shown in Tables III and IV (test 3) as averages for the entire period of operation.

It was necessary to operate the second-stage dryer with an inlet gas temperature of not over about 350° F. to avoid melting of the material in the dryer. The higher ammonium nitrate content due to the use of ammonium sulfate probably accounted for the lower melting point. The use of the lower gas temperature decreased the capacity of the Roto-Louvre dryer about 10%.

Small scale tests were made in which langbeinite (21.4% K_2O, 19.0% MgO, and 67.1% SO_4) or glaserite (41.6% K_2O, 7.1% Na_2O, and 56.5% SO_4) was used to furnish the sulfate ion for reaction with the calcium nitrate present after ammoniation of the phosphate rock–nitric acid acidulate. Langbeinite is a naturally occurring mineral. Glaserite can be produced readily from certain ores that contain langbeinite.

When using langbeinite, the quantity required to provide sufficient sulfate to react with the calcium nitrate present after ammoniation resulted in a K_2O/ P_2O_5 weight ratio of 0.29. With glaserite, the K_2O/P_2O_5 weight ratio was 0.67. In these tests the remainder of the potassium oxide to give a K_2O/P_2O_5 weight ratio of 1 was supplied in the form of potassium chloride.

Florida phosphate rock (35-mesh) containing 34.6% phosphorus pentoxide and 49.6% calcium oxide was acidulated to a HNO_3/CaO mole ratio of 1.8 with 42% nitric acid. Ammoniation was carried out batchwise with anhydrous ammonia gas to a NH_3/NO_3 mole ratio of 0.6. The sulfate mineral was added just before the start of ammoniation, and the potassium chloride was added after ammoniation was completed. The ammoniated slur-

ries were dried in a laboratory oven. The grade of the product made with langbeinite and potassium chloride was 10–10–10 (N:P_2O_5:K_2O). The grade of the product made with glaserite and potassium chloride was 11–11–11. The availability of the phosphorus pentoxide was 98% in both products.

The tests indicated that glaserite and potassium chloride can be substituted for potassium sulfate in the process without change in equipment or procedure. The drying characteristics of the product made with langbeinite appeared to be considerably different from those of the other products, and therefore, the equipment or procedure used in the pilot plant may not be suitable for operation with langbeinite.

Product Characteristics

Although extensive agronomic tests of the product obtained with potassium sulfate (12–12–12) are not yet completed, the results obtained thus far, and the results of greenhouse tests, indicate the product to be as effective as commercial-type mixtures or as ammonium nitrate, concentrated superphosphate, and potassium chloride when these materials are used to supply equivalent amounts of nitrogen, phosphorus pentoxide, and potassium oxide.

Bulk-storage tests were made by storing the product for 90 days in wooden bins, which were 10 feet high and had a cross-sectional area of 3 square feet, to simulate storage in piles having the same ratio of volume to area exposed to the atmosphere. In some tests the product was charged to the bins at 155° F. to simulate storage directly from the dryer, and in other tests the product was charged to the bins at room temperature. After 90 days there was a $1/2$-inch crust on top of the material in each bin; the crusts crumbled readily with hand pressure, and the products flowed readily through 6- by 9-inch cleanout doors at the bottom of the bins. Analyses of the products showed no increase in the moisture contents. About 1% of the contents of each bin was in the form of 2- to 3-inch lumps; these broke readily when the product was screened. In other tests the products were dry and free-flowing after 12 months of storage in 100-pound five-ply paper bags having one asphalt-laminated ply.

Tests with a John Blue No. 30 screw-type fertilizer distributor showed the products to have satisfactory drilling characteristics before and after storage.

The product made with ammonium sulfate (17–13–0) was in satisfactory condition after 12 months of storage in five-ply paper bags having one asphalt-laminated ply.

G. G. Patterson participated in the development of the process. A significant portion of the analytical work was done by R. H. Dorris and L. R. Randles.

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N-Trichloromethylthio Compounds Evaluated as Fungicides

FUNGICIDES

Preparation and Some Properties of N-Trichloromethylthiotetrahydrophthalimide

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The synthesis and properties of N-trichloromethylthiotetrahydrophthalimide have been studied in view of the current interest in this compound as a commercial agricultural fungicide. Also, 17 additional compounds containing the N-trichloromethylthio group were synthesized and evaluated for fungicidal activity. The purpose of this work was to determine whether the N-trichloromethyl group is the group primarily responsible for the fungicidal activity. The reaction of perchloromethyl mercaptan with sodium Δ^4-tetrahydrophthalimide in aqueous solution is extremely rapid. The time required for completion is largely governed by the degree of dispersion of perchloromethyl mercaptan in the aqueous phase. Rapid completion of the reaction and temperature control are important variables in obtaining high yields of captan. Temperatures higher than 20° C. and long reaction times result in side reactions involving hydrolysis of the intermediates, perchloromethyl mercaptan and sodium Δ^4-tetrahydrophthalimide. All the N-trichloromethylthio derivatives prepared in this work were found to be highly active fungicides, indicating that the N-trichloromethylthio group is the active portion of the molecule.

THE COMPOUND *N*-TRICHLOROMETHYL-THIOTETRAHYDROPHTHALIMIDE (commonly known as SR-406 or captan, the common name approved by the Interdepartmental Committee on Pest Control) is a member of a new class of highly active organic fungicides, which is cur-rently undergoing commercial development as an agricultural pesticide. This group of compounds is characterized by the $>$NSCCl₃ group, and is formed by the reaction of perchloromethyl mercaptan with imides, hydantoins, 2,4-oxazolidinediones, and certain amides and amines (*7*). Their early screening and agricultural development were conducted in a joint project with Rutgers University and New Jersey Agricultural Experiment Station staffs. This paper deals with captan, because its preparation and properties have been more