

The cylinder is a 250-ml. graduate, with scale depth approximately 21 cm., and the uppermost nine tenths of the volume is removed after the 30-minute settling period. For compliance with the specifications, the average concentration in the withdrawn layer must be at least 50% of the original. For convenience the concentration is derived from analysis of the 25 ml. of suspension and sediment remaining in the bottom of the cylinder.

The difference in water temperature makes the viscosity 20% lower than in BHC I and II, so that for accurate comparison the settling velocities should be adjusted to a common temperature. However, because of the uncertainty of effects of temperature on floccule size, and the fact that in some of the other procedures the temperature is indefinite, no attempt will be made to correct for viscosity differences.

The original concentrations for the general method are varied to suit the active ingredient. The percentage concentration for DDT, chlordane, malathion, and methoxychlor is 2.5; for dieldrin 0.625; for BHC 0.5, based on gamma isomer content only; and for Diazinon also 0.5.

In velocity range the general method presents a compromise between the relatively narrow bands of the DDT and dieldrin methods and wide range of the BHC methods. The new range is 0 to 19 cm. in 30 minutes, or 0 to 38 cm. per hour. The specification requirement means that the average height of the curve over the range from the origin to G shall be not less than 50%. The sample represented meets this requirement, with a little to spare.

Discussion

The high-suspensibility type of water-dispersible insecticide powder is one in which nearly all components have settling velocities no higher than the order of 1 cm. per minute. In this connection velocity is not expressible in terms of a specific particle size, but is a characteristic of prime interest for itself alone. In terms of the cumulative settling-velocity distribution curve, this means a high plateau beginning in or before the vicinity of 60 cm. per hour.

Each of the specification test requirements seeks in its own way to bolster the curve by supporting it at some place in or preceding this vicinity. The DDT and dieldrin methods tackle the curve at fairly definite points, the former holding the percentage up to 60 (usually) at 14 cm. per hour and the latter to 70 at 20 cm. per hour. The BHC methods (I and II) and the WHO general method use a more generalized approach, maintaining a minimum average height over roughly the entire preplateau region; the minimum average heights (cumulative percentages) and the ranges over which they are ensured by the respective methods are 75% from 0 to 90 cm. per hour, 65% from 0 to 84 cm. per hour, and 50% from 0 to 38 cm. per hour.

The way in which these diverse methods fit together into a pattern suggests what may be a more direct approach to their common purpose. In terms of guarantees for effective life of un-reagitated suspension, these methods act by regulating various features of the final sharply deteriorating phase. One wonders if it would not be simpler and equally effective to regulate this

unsatisfactory phase merely by making it as brief as possible. Instead of stipulating how low a level of performance will be tolerated at certain stages of the failure period, or in overall average for this period, we might set a minimum limit on duration of good performance, ignoring the details of the unavoidable drop at the end. The criterion would be established with regard to the shoulder of the curve. A suggested requirement based on this aspect is not less than 90%, under 60 cm. per hour.

Acknowledgment

The authors are grateful for helpful suggestions received from Irvin C. Brown, of the Soil and Water Conservation Research Branch, in the preparation of this paper.

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Received for review October 26, 1955. Accepted January 18, 1956. Work conducted in part under funds allotted by the Department of the Army to the Department of Agriculture.

AMMONIUM METAPHOSPHATE FERTILIZER

Pilot Plant Production and Greenhouse Tests of Fertilizer from Ammonia and Phosphorus Pentoxide Vapors

PRODUCTION OF A CONCENTRATED NITROGEN-PHOSPHATE FERTILIZER directly from ammonia and phosphorus pentoxide was studied by the Tennessee Valley Authority as a part of its search for new and improved fertilizers. The work resulted in the development of a process for the production of a fertilizer containing 90% plant food (17% nitro-

gen and 73% phosphorus pentoxide). The process consists of burning phosphorus with dried air, making the resultant gas containing phosphorus pentoxide vapor react with ammonia at elevated temperatures, and hydrolyzing the product from this reaction with steam.

Other investigators also have studied the reaction of ammonia and phosphorus pentoxide. Ross, Merz, and Carothers (8) reported the production of a fer-

tilizer from the reaction of ammonia and phosphorus pentoxide in the presence of water but did not give sufficient information to permit defining the requirements of the process. The product obtained in their investigation was a light, fluffy powder, and they postulated that it was a mixture of ammonium metaphosphate, ammonium orthophosphate, and ammonium pyrophosphate. Rice (6, 7) also published information on the reaction of ammonia and phosphorus

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A continuous process for the production of a highly concentrated fertilizer from ammonia and phosphorus pentoxide was studied on a pilot plant scale. Phosphorus was burned with dried air, the resultant gas containing phosphorus pentoxide vapor reacted with ammonia at temperatures of 600° to 1000° F., and the product from this reaction was hydrolyzed at about 250° F. with steam. The final product was granular, contained about 17% nitrogen and 73% phosphorus pentoxide, and was relatively nonhygroscopic. It was predominantly ammonium metaphosphate; the remainder was complex nitrogen-phosphorus compounds. Other methods for processing the products from the reaction of ammonia and phosphorus pentoxide to obtain final products of satisfactory properties were identified. Potash was added during the hydrolysis step in some tests to produce N-P₂O₅-K₂O fertilizers. Greenhouse studies using Sudan grass, red clover, and rye grass indicated that the experimental products were effective fertilizers. The crop response to phosphate was equal to or better than to phosphate in concentrated superphosphate or calcium metaphosphate fertilizers. The experimental products were nitrified more rapidly than ammonium sulfate.

pentoxide in the presence of water, but made no reference to the suitability of the product as a fertilizer.

Woodstock (9) reported laboratory studies of the reaction of gaseous and liquid ammonia with solid phosphorus pentoxide in an oil suspension. He reported nitrogen-phosphorus pentoxide complexes of nitrogen-phosphorus atomic ratios of 1.25:1 to 1.5:1 suitable for use as a water softener, but made no reference to their use as fertilizers.

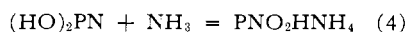
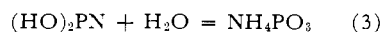
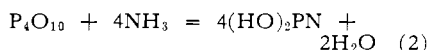
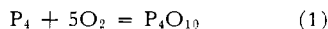
Information was published by Jones and Arvan (5) on the reaction of ammonia and phosphorus pentoxide in a dry system at the conclusion of the authors' reported studies. Their work was apparently similar to some of that carried out in initial studies of the present investigation. They stated that their materials were suitable for use as fertilizers, water softeners, and flameproofing compounds.

Exploratory Studies

The initial studies made by TVA of the reaction of ammonia and phosphorus pentoxide were carried out in laboratory equipment (2, 3). The most promising results were obtained when ammonia reacted with phosphorus pentoxide vapor in a "dry system" at elevated temperatures. The phosphorus pentoxide vapor was prepared by the combustion of phosphorus with dried air, which was used to minimize the formation of metaphosphoric acid. The product from this reaction was a light, fluffy powder (bulk density of 15 pounds per cubic foot), which contained about 17% nitrogen and 80% phosphorus pentoxide.

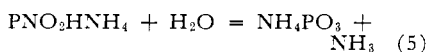
X-ray diffraction patterns and microscopic examination indicated that the major portion of the product was an ammonium metaphosphate. When it reacted with acetylene tetrachloride, phosphonitrilic chloride was formed, which confirmed the presence of some

phosphonitrilic compound (PN radical). Typical products contained nitrogen and phosphorus in atomic ratios of about 1.1 to 1 with from 70 to 77% of the nitrogen in ammoniacal form. It was postulated they were mixtures of 70 to 75% ammonium metaphosphate, NH₄PO₃; 10 to 15% ammonium phosphonitride, PNO₂HNH₄; and 10 to 20% phosphonitridic acid, (HO)₂PN. The reactions postulated are represented by Equations 1, 2, 3, and 4.



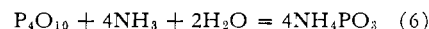
A small pilot plant was constructed to study further the process as defined in the laboratory. It was planned to compress the light, fluffy material to increase its bulk density and particle size. The products obtained in the pilot plant had nitrogen-phosphorus atomic ratios of 1.1:1 to 1.2:1 and contained 16 to 19% nitrogen and 74 to 79% phosphorus pentoxide. Calculations indicated that they contained 60 to 70% ammonium metaphosphate. However, when exposed to air at 70% relative humidity and 86° F., they were too hygroscopic to be satisfactory for fertilizer material.

In further explorations it was found that relatively dense (40 to 50 pounds per cubic foot), nonhygroscopic products containing 80 and 95% ammonium metaphosphate, respectively (Table I), could be obtained by treating the light, fluffy material with steam at elevated temperatures or by permitting it to absorb moisture and then heating it (Equations 3 and 5).



Other methods for obtaining products of satisfactory properties also were identi-

fied. Heating the material from the dry system in the absence of moisture increased its bulk density to about 40 pounds per cubic foot (-6 +35 U. S. screen size), but did not increase its ammonium metaphosphate content or decrease its hygroscopicity to the same extent as heating in the presence of moisture (see Table I). Adding water vapor at the point of reaction between the ammonia and phosphorus pentoxide vapor in amounts between 130 and 200% of the stoichiometric requirement to form ammonium metaphosphate (Equation 6)



resulted in products that contained 90 to 95% ammonium metaphosphate and were relatively nonhygroscopic (Table I). However, they were of minute particle size and low bulk density.

An unusual characteristic of all the products was that they formed gels when mixed with water. This characteristic interfered with the AOAC procedures for determining the proportions of nitrogen and phosphorus that were in water-soluble forms, because the gels could not be filtered in the prescribed time even when suction was applied. Consequently, the water solubilities of these constituents were determined by (1) agitating a 1-gram sample in 250 ml. of water for 1 hour, (2) filtering a portion of the supernatant liquid, and (3) analyzing the filtrate by AOAC procedures. By this modified procedure, 90 to 100% of the nitrogen and phosphorus in the material produced by the reaction of ammonia and phosphorus pentoxide vapor in the presence of moisture were in forms soluble in water in 1 hour. From 40 to 60% of the nitrogen and phosphorus in the products from the dry system, including those obtained by heating and by hydrolyzing and heating, were

Table I. Chemical and Physical Properties of Exploratory Products

Material	Ammonium Metaphosphate Produced from Dry-System Product				Ammonium Metaphosphate Produced by Reacting Ammonia and Phosphorus Pentoxide at 650° F. in Presence of Moisture	
	Dry-System Product	Heating, 450° F., 30 min.	Adding water (10% by wt.) and heating 450° F., 30 min.	Reacting with steam, 200° F.	Moisture	
					As produced	After heating, 450° F., 30 min.
	1	2	3	4	5	6
Chemical analysis, wt. %						
Nitrogen						
Total	17.5	16.3	14.5	16.7	15.3	14.4
Ammoniacal	12.2	11.9	13.6	13.8	13.6	14.1
P ₂ O ₅						
Total	76.0	77.4	73.5	73.1	70.5	72.8
Availability	84.3	34.4	28.6	93	99.9	72.1
N:P atomic ratio	1.17	1.07	1.00	1.16	1.10	1.00
Ammoniacal N:total N atomic ratio	0.70	0.73	0.94	0.83	0.89	0.98
Ammonium metaphosphate content (calcd.), %	67	73	95	81	89	98
Water solubility, %						
1 hour	40	40	50	60	100	90
24 hours	Completely	Completely	...	Completely
1 month	Completely
6 months	Completely
1 year	...	67
Bulk density after crushing to -6 + 35 screen size (U. S.), lb./cu. ft.	15	40	40	50	15	20
Appearance	Powdery	Granular and friable	Hard and granular	Extremely hard and granular	Powdery	Powdery
Hygroscopicity test results after exposure at 70% relative humidity and 86° F., 1 hour, H ₂ O adsorbed, wt. %						
Condition	17.6 Gummy	9.4 Gummy	2.6 Dry and granular	1.5 Dry and granular	16.1 Dry and powdery	0.7 Dry and powdery

in soluble forms; the remaining portions of the nitrogen and phosphorus were not soluble in 1 hour by the procedure used. The results of the water-solubility studies are shown in Table I.

Because of the difficulty in filtering, the proportion of phosphorus in a citrate-soluble form was determined by the AOAC procedure for nonacidulated materials, which did not involve extraction with water (7). In some cases the amounts of phosphorus in a citrate-soluble form were reported to be less than the amounts in a water-soluble form. The higher concentration of the ammonium

ion in the neutral ammonium citrate solution than in water apparently retarded the solubility of these materials in the citrate solution through a common ion effect. By this method of analysis, the proportions of phosphorus in citrate-soluble forms ranged from 29 to 99.9% (Table I). The phosphorus in products obtained from the wet system and from the dry system, with and without subsequent treatment with steam, was in forms that were highly citrate-soluble; the phosphorus in the material formed by heating and by adding water to and heating the product from the dry system had low

citrate solubilities. However, greenhouse tests showed that these values for citrate solubility were not indicative of the phosphorus fertilizer values of the products, since crop responses were equal to or better than obtained with concentrated superphosphate or calcium metaphosphate.

Greenhouse Tests

The materials produced in the exploratory tests were tested in the greenhouse to determine their fertilizer effectiveness.

Table II. Effectiveness of Phosphorus in Experimental Ammonium Metaphosphate Fertilizers

Material ^b	Method of Preparation	Screen Size, U. S. Sieve Series	Crop Yields ^a , Grams (Dry Wt.)				Av. of Yields from All Crops, Grams (Dry Wt.)
			Clarksville Silt Loam, pH 6.5		Hartsells fine sandy loam, pH 6.5, red clover	Clarksville silt loam, pH 5.5, rye grass	
			First crop, Sudan grass	Second crop, rye grass			
1	Dry-system product	Powder, as produced	11.2	4.5	13.2	13.3	10.6
2	1 + heat	-12 +35	13.2	4.9	14.7	13.8	11.7
3	1 + water + heat	-12 +35	14.5	5.2	15.0	14.6	12.3
4	1 + steam	-6 +12	14.4	5.5	15.7	14.2	12.5
		-12 +35	14.4	5.2	14.5	14.5	12.2
		-35	11.2	4.4	13.0	12.5	10.3
5	Wet-system product	Powder, as produced	12.0	4.7	14.5	13.3	11.1
6	5 + heat	Power, as produced	12.6	4.3	14.9	14.3	11.5
Controls							
Calcium metaphosphate		-100	11.5	4.2	14.1	13.6	10.9
Concentrated superphosphate		-20	10.1	4.5	14.6	13.0	10.6
None			3.4	1.6	8.3	4.0	4.3
LSD (0.05)			1.6	...	1.2	1.2	...

^a Average for yields from 40 and 80 pounds of P₂O₅ per acre applications.

^b For chemical analyses and descriptions of products see Table I.

Nitrification tests showed that the experimental materials nitrified more rapidly than ammonium sulfate. After 112 days, 59% of the ammonium sulfate and 71 to 91% of the ammonium metaphosphates had nitrified. From these data it can be assumed that the materials are effective sources of nitrogen for plants. Other studies of the fertilizer effectiveness of the nitrogen in these materials are planned.

Results of studies of the effectiveness of the phosphorus in the materials are summarized in Table II. Three different soil conditions were used. Sufficient ammonium sulfate was added to supply a constant amount of nitrogen in all instances, and potassium chloride was added to supply potassium. In one experiment, Sudan grass was grown as a first crop, followed by rye grass to measure the residual effects of the materials. In two other experiments, red clover and rye grass were grown.

More plant growth was obtained with the materials produced by (1) the steam-treatment method (material 4, -6 +12, and -12 +35 screen size) and (2) allowing the dry-system product to absorb moisture and then heating it (material 3) than with the other experimental materials or the controls. With the first crop, Sudan grass, the yields from these hydrolyzed materials were significantly greater (25 to 45%) than the yields from the calcium metaphosphate and concentrated superphosphate controls. With the second crop, rye grass, the yields from these hydrolyzed materials were not significantly greater (10 to 25%) than from the controls. The plant growth from the other experimental materials was not significantly different than from the controls.

In the experiments in which single crops of red clover and rye grass were grown, the yields from essentially all the experimental products were not significantly different from the controls; the only exceptions were the yields from material 1 and the fine particle size from material 4, which were significantly less than the calcium metaphosphate in the red clover experiment.

In a test of the effect of particle size (material 4), higher yields were obtained with the +35 than with the -35 screen size product.

Pilot Plant Development of Steam-Treatment Process

The process in which the product of the dry system was treated with steam appeared more promising technically and resulted in the production of a material which gave the best results in the greenhouse studies. Therefore, it was studied more extensively on a pilot plant scale. A description of the process as developed in the pilot plant studies and the effects of variables studied are given

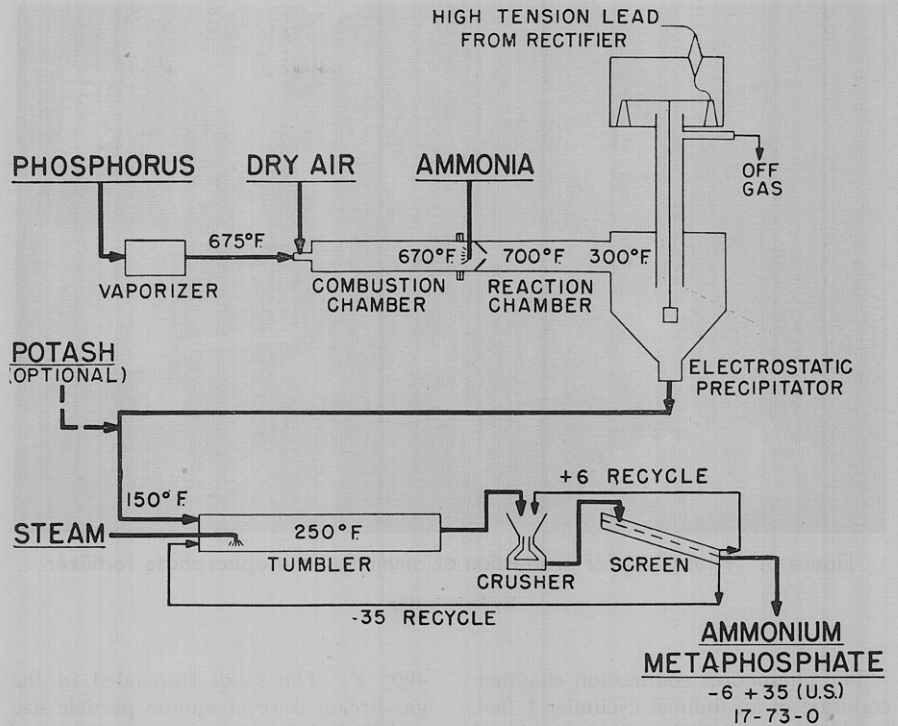


Figure 1. Flowsheet of pilot plant for production of ammonium metaphosphate fertilizer

below. A flow sheet of the process (Figure 1), and photographs of the pilot plant equipment (Figures 2 and 3) are shown.

Description of Process

(1) burning phosphorus with dried air in a combustion chamber to produce phosphorus pentoxide vapor, (2) making phosphorus pentoxide vapor react with gaseous ammonia at temperatures of 600° to 1000° F. in a reaction chamber to produce a solid "intermediate" product of desired nitrogen-phosphorus atomic ratios, (3) collecting this intermediate material in an electrostatic precipitator, (4) hy-

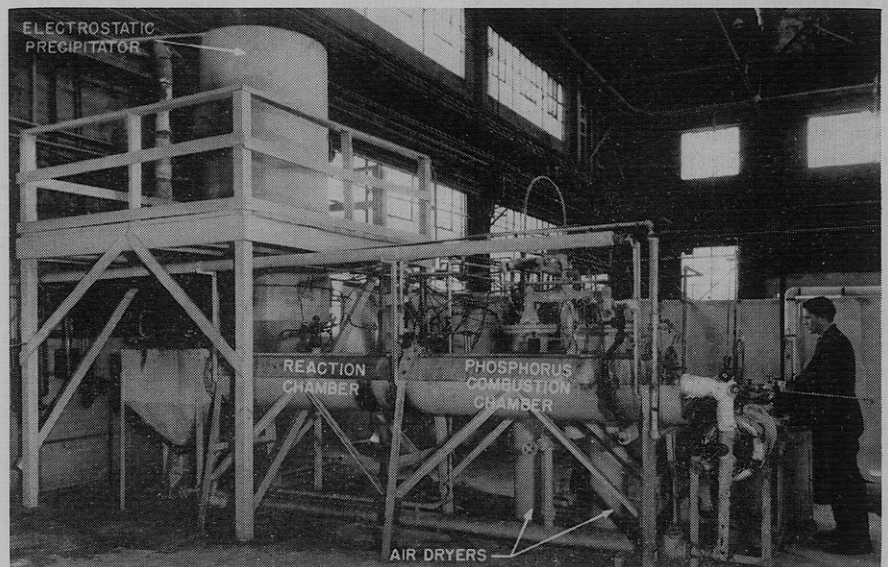
drolyzing and agglomerating it in a rotary tumbler at about 250° F. with steam, and (5) crushing and screening final product.

The pilot plant equipment did not permit continuous integrated operation. Phosphorus was burned at rates of 6 to 10 pounds per hour, resulting in production of 18 to 30 pounds of intermediate product per hour. Hydrolysis was carried out at 110 to 170 pounds per hour.

Combustion of Phosphorus White phosphorus of 99.5% purity was metered and vaporized in standard equipment, described in previous TVA studies (4).

Figure 2. Pilot plant for production of ammonium metaphosphate fertilizer

Ammonia-phosphorus pentoxide reaction step



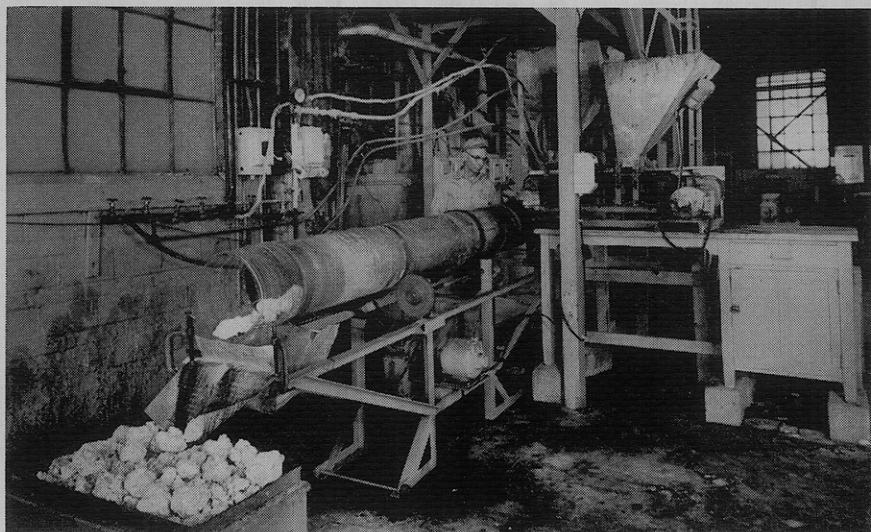


Figure 3. Pilot plant for production of ammonium metaphosphate fertilizer

Hydrolysis step

The phosphorus combustion chamber consisted of an unlined cyclinder 1 foot in diameter by 6 feet long, made of A.I.S.I. Type 316 stainless steel. Phosphorus vapor from an electrically heated vaporizer was introduced through a 1-inch pipe at one end of the chamber; dried air was introduced tangentially around this pipe for combustion of the phosphorus and for cooling the resultant phosphorus pentoxide before it entered the ammonia-phosphorus pentoxide reaction chamber. The air for combustion was dried to about 0.0003 pound of water per pound of dry air in towers packed with silica gel. The phosphorus burning rate usually was about 7 pounds per hour and the amount of air usually was 400% in excess of that required for burning the phosphorus. Under these conditions of operation the moisture in the air theoretically would react with 3% of the phosphorus to form metaphosphoric acid. Deposits high in metaphosphoric acid content were found in the combustion chamber.

Ammonia-Phosphorus Pentoxide Reaction

The ammonia-phosphorus pentoxide reaction chamber for the production of the intermediate product was essentially an extension of the phosphorus combustion chamber. It was 1 foot in diameter and about 6 feet long and was made of mild steel. Gaseous ammonia was introduced through a circular-pipe distributor located 4 inches from the junction of the combustion chamber and reaction chamber. A conical baffle was located downstream from the ammonia inlet to increase the contact between the ammonia and phosphorus pentoxide vapor.

The shell of the reaction chamber was cooled with water to reduce the temperature of the gas and solids entering the electrostatic precipitator to 200°

F. The solids suspended in the gas stream were of minute particle size and the mixture had the appearance of cigarette smoke.

The reaction of the ammonia and phosphorus pentoxide was carried out at temperatures of from 400° to 1000° F. The amount of air used for combustion of the phosphorus was varied from about 200 to 400% in excess of that required for burning the phosphorus. Varying the temperature or amount of combustion air in these ranges had no apparent effect on the appearance, hygroscopicity, or chemical composition of the intermediate material. There was evidence that the amount of excess ammonia required to carry out the reaction decreased with an increase in temperature and a decrease in the amount of combustion air used; these effects are now being studied. It is possible that the beneficial effects of decreasing the amount of combustion air were derived from increasing the partial pressure of ammonia.

Normally, sufficient ammonia was introduced to produce intermediate material of nitrogen-phosphorus atomic ratios of from about 1.1:1 to 1.2:1. At a temperature of 1000° F. and with 300

to 400% excess air for combustion of the phosphorus, a 1.1 to 1 ratio product was obtained when the proportion of ammonia was 7% in excess of that which reacted; a 1.2 to 1 ratio product was obtained when the proportion of ammonia fed was about 30% more than that which reacted. There was no evidence of cracking of ammonia in the system.

Typical operating data for production of the intermediate material are shown in Table III; a typical chemical analysis of the material is shown in Table IV.

Collection of Intermediate Product

The electrostatic precipitator for collection of the intermediate product was about 11 feet in height and 4 feet in diameter and had a cone bottom. The gas stream entered the side of the precipitator and passed through a 12-inch pipe, which was about 5 feet long and was mounted inside the outer shell. A 1/4-inch steel rod was hung so that it was suspended in the center of the pipe. A strong electrical field was maintained between the rod, which served as the discharge electrode, and the pipe, which served as the collecting electrode. The solids collected on the inner surface of the pipe; the pipe was vibrated intermittently and the solids dropped to the bottom of the precipitator, from which they were removed periodically. The intermediate product was bagged immediately to prevent it from absorbing moisture, and stored for subsequent use in the hydrolysis step.

The equipment used to produce the strong electrical field necessary to collect the product consisted of a transformer, which stepped up the line voltage from 440 volts to from 55,000 to 75,000 volts, and a mechanical rectifier, which converted the alternating current to unidirectional current. Generally, the precipitator was operated at 55,000 volts and the current between the discharge and collecting electrodes was less than 3 amperes. Under these conditions of operation less than 1% of the phosphorus input to the pilot plant was contained in the gases leaving the precipitator.

Table III. Typical Pilot Plant Data for Production of Intermediate Product

Phosphorus feed rate, lb./hr.	6.5	9.8
Ammonia feed rate, cu. ft./min. (N.T.P.)	2.7	2.5
Combustion air flow, cu. ft./min. (N.T.P.)	45	30
Moisture content of combustion air		
Dew point, ° F.	-21	-18
Lb. H ₂ O/lb. dry air	0.00033	0.00039
Temperature, ° F.		
Phosphorus melter	150	150
Phosphorus vaporizer	700	760
Combustion chamber	720	1,170
Reaction chamber	760	1,000
Electrostatic precipitator		
Secondary voltage tap, volts	55,000	55,000
Amperes	2.5	2.5

Hydrolysis of Intermediate Product

The rotary tumbler used in the hydrolysis step of the process was 1 foot in diameter and 8 feet long. The intermediate product was fed from a belt feeder into a chute entering the tumbler. Steam for the reaction was introduced through a 1/2-inch pipe which extended 18 inches

the product was allowed to cool to room temperature and then was crushed to -6 +35 screen size (U. S. sieve series). The -35-screen size material from the tumbler and from the crushing operation was recycled to the tumbler and agglomerated.

The best temperature for the reaction of the steam and the intermediate product was in the range of 225° to 275° F. At reaction temperatures above 300° F. material stuck to the walls of the tumbler, even when the tumbler was cooled with water. At reaction temperatures below 225° F., the bulk density of the material obtained was low (30 pounds per cubic foot or less).

Final products of acceptable physical properties and containing at least 80% ammonium metaphosphate were obtained when the amount of water added as steam was in the range of 100 to 150% of that required for the reaction represented by Equation 6. When less than about 100% of the theoretical amount of steam was used, the product contained less than 80% ammonium metaphosphate and was hygroscopic. When more than about 175% was used, the bulk density was only 15 pounds per cubic foot.

Incorporation of Potash A few exploratory tests showed that potash could be incorporated during hydrolysis of the intermediate product to produce granular three-component fertilizers. Materials were

prepared which contained up to 30% potassium oxide (10% nitrogen, 40% phosphorus pentoxide, and 30% potassium oxide). Ammonium metaphosphate also was readily amenable to dry mixing with potash to produce various N:P₂O₅:K₂O ratios.

Properties The product obtained by the reaction of ammonia and phosphorus pentoxide vapor in a dry system, followed by hydrolysis with steam, was granular and relatively non-hygroscopic and, when sized to -6 +35 U. S. screen size, had a bulk density of 40 to 45 pounds per cubic foot. It analyzed about 17% nitrogen and 73% phosphorus pentoxide and contained 80 to 86% ammonium metaphosphate. About 20 to 30% of the nitrogen and phosphorus were in forms that were slowly soluble in water; from 96 to 99% of the phosphorus was citrate-soluble.

Bag-storage tests were made in an unheated building with windows open to simulate open warehouse storage. The product, as discharged from the rotary tumbler, contained less than 1% free moisture. It was bagged in five-ply paper bags having one asphalt-laminated moistureproof ply. Each bag contained about 65 pounds of material (1.5 cubic feet). The bags were placed in the fourth, eighth, and twelfth positions from the top of a 12-bag stack; the other positions were filled with bags containing 100 pounds of sand.

Inspection of the bags after 6 months of storage showed that there was only a slight bag set, which broke up when the bags were moved from their positions. There were no lumps present, and the material was dry and free flowing.

Table IV. Typical Chemical Analyses of Intermediate Product and Ammonium Metaphosphate Fertilizer Produced in Pilot Plant Operation

	Analysis, Wt. %	
	Intermediate product	Ammonium metaphosphate fertilizer
Nitrogen, %		
Total	18.3	16.7
Ammoniacal	12.9	13.8
Water-soluble	11.0	11.7
Water-soluble N, % of total N	60	70
Ammoniacal N:total N atomic ratio	0.70	0.83
P ₂ O ₅ , %		
Total	76.8	73.4
Available	76.0	70.7
Water-soluble	46.3	51.2
Availability, % of total P ₂ O ₅	99.0	96.5
Water-soluble P ₂ O ₅ , % of total P ₂ O ₅	60	70
Product N:P atomic ratio	1.21	1.14
Ammonium metaphosphate content (calcd.), %	66	81

into the tumbler and was fitted with a 90-degree elbow and nipple to direct the steam flow onto the bed of material in the tumbler; the end of the pipe nipple was about 3 inches from the bed. A 2-inch retaining ring was mounted in the feed end of the tumbler and a 3/4-inch ring was located 6 inches beyond the point at which the steam entered.

Typical operating data of the hydrolysis step are shown in Table V. The tumbler normally was operated at speeds of 20 to 30 r.p.m. and at feed rates of 110 to 170 pounds per hour. The retention time of the material in the tumbler was about 2 minutes. In passing through the tumbler, the material was first heated to a temperature of about 150° F. by means of a burner located at the feed end of the tumbler. Where the material came into contact with the steam, its temperature increased rapidly to about 250° F. and it agglomerated into lumps up to 6 inches in diameter. Cooling water was used on the exterior of the tumbler shell at the point of introduction of the steam to prevent material from sticking to the walls of the tumbler. About 2 to 6% of the nitrogen input was lost during hydrolysis.

On discharging from the tumbler,

Table V. Typical Pilot Plant Data for Hydrolysis of Intermediate Product

Operating conditions		
Hours operated	8.1	10.8
Tumbler rotation speed, r.p.m.	30	30
Reaction product fed		
Lb.	918.0	1828.5
Lb./hour	113	170
Steam rate		
Lb./hour	17.3	22.5
% of theoretical required to form NH ₄ PO ₃ ^a	150	137
Temperatures, ° F.		
Feed	150	175
At steam inlet	250	270
Product	310	280
Product		
Weight, lb.	972	1887
Bulk density after crushing to -6 +35 screen size, lb./cu. ft.	42	41.5
Screen analysis after crushing, wt. % (U. S. sieve series)		
-6 +12	58.1	51.7
-12 +20	22.3	26.8
-20 +35	15.4	17.2
-35	4.2	4.2
Nitrogen loss during hydrolysis, % of total N	6.6	2.8
% nonammoniacal nitrogen converted to ammoniacal nitrogen	24.1	29.4

^a According to reaction: P₄O₁₀ + 4NH₃ + 2H₂O = 4NH₄PO₃.

Conclusions

The production of a high-analysis, relatively nonhygroscopic, granular fertilizer from ammonia and phosphorus pentoxide vapor was demonstrated on a pilot plant scale. The fertilizer contained about 17% nitrogen and 73% phosphorus pentoxide, a total of 90% of plant food; calculations indicated that it contained 80 to 86% ammonium metaphosphate. About 20 to 30% of the nitrogen and phosphorus were present in forms slowly soluble in water. The process consisted of burning phosphorus with dried air, making the resultant gas containing phosphorus pentoxide vapor react with ammonia, and hydrolyzing the product from this reaction with steam. Potash was added during the hydrolysis step in some of the tests to produce N-P₂O₅-K₂O fertilizers. Other methods for processing the product of the reaction of ammonia and phosphorus pentoxide vapor to produce fertilizers of acceptable physical properties also were identified.

Greenhouse studies using Sudan grass, red clover, and rye grass indicated that

all the experimental products were effective fertilizers. The crop response to phosphate was equal to or better than that obtained from the phosphate in either concentrated superphosphate or calcium metaphosphate fertilizers. Nitrification studies showed that the experimental products were nitrified more rapidly than ammonium sulfate.

Field tests of the steam-treated material produced in pilot plant operation are under way in 11 states as far west as Utah and as far north as New York.

Acknowledgment

The authors acknowledge the advice and guidance of T. P. Hignett, who was

in administrative charge of the project. S. C. Blalock and E. T. Tonn participated in the engineering studies. The greenhouse tests were conducted by the Tennessee Agricultural Experiment Station under a cooperative agreement with TVA. A significant portion of the analytical work was carried out by D. R. Miller and L. J. Sheffield.

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Received for review September 14, 1955. Accepted January 17, 1956.

NUTRITIVE QUALITY OF CROPS

Methionine Content of Soybeans as Influenced by Location and Season

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Results obtained in this study indicate differences in methionine content of protein in soybean varieties. Strains from Dunfield crosses and the strain Clark were superior to other strains tested. The strain Clark was significantly higher in methionine content than either of its parents, indicating transgressive segregation within the Lincoln \times Richland cross. It should be possible to develop varieties high in methionine content by plant breeding. There were significant seasonal variations only in Group IV, methionine being generally higher in 1952 than in the two previous years. The variation which could be attributed to location effect was not consistent enough to show significance at the 5% level except in Group III. These results indicate that soybean protein is produced in the seed with variable proportions of amino acids.

SOYBEANS have become our most important source of vegetable protein and many feeding experiments have shown that soybean protein is deficient in methionine. The purposes of this investigation were to determine whether there are differences in the methionine content of different lots of soybean protein, the factors influencing methionine content, and the feasibility of breeding soybeans with higher methionine content. A 3-year study was made of samples of 14 soybean varieties, each grown at from 12 to 18 locations composited by variety and by location. In most cases, season and location were not consistent enough in their effect to be significant, but there were definite genetic differences indicating that it should be possible to increase methionine in soybean protein by breeding.

Our greatest source of protein for livestock feeding is soybean oil meal. Although there are surpluses of many agricultural commodities, there is a

potential demand for about twice as much soybean protein as is now being produced (6). It would be possible to effect the equivalent of an increase in protein for animal feeding, without increasing the quantity produced, if certain amino acid deficiencies could be overcome.

The proportions of amino acids in soybean protein as reported by Block and Bolling (3) and Alderks (7) come remarkably close to matching requirements for rat growth as reported by Rose (72). However, the nutritional value of the protein is limited by a deficiency in the proportion of methionine and cystine present, as shown by Flodin (4) in his report on amino acid balance in protein. Cystine is included with methionine, because experiments have shown that, to a limited extent, methionine deficiency may be alleviated by supplying cystine (74). These data should be considered as only indicative and subject to revision, in view of the limited accuracy of

existing information both on protein composition and on amino acid requirements of animals. Final proof is obtained in actual feeding trials, many of which have shown that soybean protein is deficient in methionine.

Soybean and corn proteins tend to supplement each other in a mixed feed, but corn protein is not high enough in methionine plus cystine to make up this deficiency in the soybean, and soybean protein is not high enough in lysine to make up this deficiency in the corn protein. As corn protein is very deficient in lysine, a mixed feed composed of corn and soybean meal is deficient in lysine; therefore higher lysine in soybean protein would be desirable. Synthetic lysine has recently become available commercially, but the high cost and high animal requirement make it an expensive supplement.

Many of the problems of availability of amino acids in soybean protein have been solved by nutritional research. Proper