

Table I. Recovery of IPC by Basic Hydrolysis

IPC Hydrolyzed, γ	IPC Recovered, γ	Recovery, %
60	54.9	91.5 \pm 0.14
100	88.3	88.3 \pm 4.7
200	187.4	93.7 \pm 2.1
400	375.9	94.0 \pm 2.2
		Av. 92.4 \pm 3.9

are involved in the hydrolysis. Read the concentration of aniline from the standard curve and calculate the concentration of IPC from the following: p.p.m. of IPC = p.p.m. of aniline \times 1.93 \times K , where K = dilution factor = 100 ml./ml. distillate for analysis.

To test the validity of this method, a series of tests of recovery of IPC involving no crops was performed (Table I).

After this procedure was established, the applicability of the method to direct

determination of IPC in plant tissue was determined. One hundred micrograms of IPC was added to 100 grams of strawberries and the recovery was determined by hydrolysis of the plant tissue. Untreated berries were hydrolyzed in the same manner to determine the control correction factor. Out of eight determinations, the average recovery was 97.5% with a standard deviation of 2.9%.

This compares favorably with recoveries of 95 and 89% reported by other methods (7, 4). The distillate of untreated strawberries gives a small and uniform absorbance. This correction factor is equivalent to 0.05 p.p.m. of IPC.

The method was satisfactory for concentrations as low as 0.1 p.p.m. In using a 100-gram sample of plant tissue for hydrolysis and 40-ml. aliquot of the distillate, the method will determine a concentration of 0.1 p.p.m. in the plant tissue. If greater sensitivity is desired, larger samples can be used and extrac-

tions carried out by the method of Bissinger and Fredenberg (7). Determinations are then made after evaporation of the solvent.

The direct hydrolysis of plant tissue has been applied only to strawberries. Its applicability to other plant tissues can be ascertained only by experimental work.

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FERTILIZER TECHNOLOGY

Concentrated Fertilizer Material from Phosphorus, Air, and Ammonia

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A method was developed on a bench scale for producing a concentrated fertilizer containing phosphorus-nitrogen bonds by burning phosphorus with dry air and treating the fume with ammonia. The product, which contains about 17% nitrogen and 80% phosphoric oxide, is probably a mixture of ammonium metaphosphate, phosphoronitric acid, and ammonium phosphoronitrate. It dissolves and hydrolyzes slowly in water. Greenhouse tests show that it is an effective source of nutrient phosphorus and nitrogen.

TWO PRINCIPAL PLANT-FOOD ELEMENTS, phosphorus and nitrogen, are directly bonded in phosphonitric compounds. Certain properties of these compounds, as reported by Stokes (10-12) and by Audrieth, Steinman, and Toy (2, 3), suggested preliminary plant culture tests. Some of the compounds proved to be good sources of nutrient phosphorus and nitrogen.

Preparation of the phosphonitric compounds in essentially pure species has generally involved indirect methods (2, 3) that are too costly for use in the production of fertilizers. A more direct method was sought.

Products that probably contained phosphonitric compounds were prepared by several investigators (4-8, 13)

through reaction of phosphorus pentoxide with ammonia under various conditions. In this approach, phosphorus vapor was burned in air, and the resultant phosphorus pentoxide was ammoniated immediately downstream from the burner. The primary factors affecting the process were evaluated, and the products were fairly well characterized.

The apparatus is shown in Figure 1. Molten phosphorus was water-pumped into a vaporizer which was held at 405° \pm 5° C. The metal parts of the apparatus were Type 316 stainless steel. The collecting train comprised a 55-gallon drum, a 30-gallon drum, and a glass electrostatic precipitator.

Variables Studied

The variables that most affect the

process are the temperature of the ammoniation reaction, and the ratio of ammonia to phosphoric oxide admitted to the system. In this study it was found also that the distance between the phosphorus flame and the ammonia sparger was important; best results were obtained when the sparger was about 7 inches below the top of the reaction chamber.

The temperature in the reaction chamber was controlled by regulating the amount and temperature of the combustion air, and in some tests, by external cooling of the combustion chamber with a water coil fitted snugly around it. The proportion of combustion air was varied in the range of three to four times that required to burn the phosphorus to phosphorus pentoxide. In tests in which water vapor was admitted to the reaction system,

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Figure 1. Apparatus for phosphoric oxide-ammonia reaction

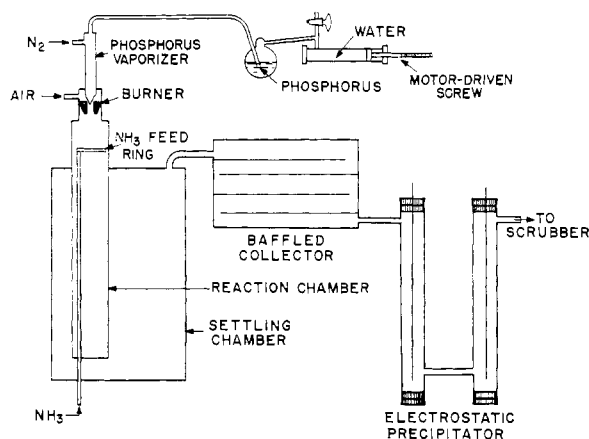


Table I. Reaction of Phosphorus Vapor, Dry Air, and Ammonia

Reaction Chamber Temp., ° C.	Input Mole Ratio		Composition of Product					
			Wt. %			Mole Ratio		
			P	Total N	NH ₃	Tot. N:P	NH ₃ :N: tot. N	
265	1.25	10.0	36.2	16.1	12.6	0.98	0.78	
285	1.40	7.5	36.2	15.6	11.3	0.95	0.72	
295	1.25	10.0	37.0	15.2	11.2	0.91	0.74	
315	1.25	10.0	36.4	17.2	12.5	1.05	0.73	
	1.40	10.0	35.8	17.5	12.2	1.08	0.70	
320	1.33	7.5	36.8	17.3	12.0	1.04	0.69	
330	1.08	10.0	36.8	16.5	11.3	0.99	0.68	
345	1.25	10.0	36.6	17.2	11.9	1.04	0.69	
	1.05	7.5	36.8	15.8	11.8	0.95	0.75	
350	1.15	7.5	37.2	15.6	11.2	0.93	0.72	
355	1.20	7.5	36.0	15.9	12.2	0.98	0.77	

steam was added at a measured rate to the dried combustion air.

Analytical Procedures

Samples of reaction products used in the determination of phosphorus and total nitrogen were digested with boiling sulfuric acid to decompose nitrilic compounds. Phosphorus was determined by the volumetric molybdate method and nitrogen by the Kjeldahl method (7). Ammoniacal nitrogen was determined (approximately) on undigested samples by the magnesium oxide method (7). The values obtained for ammoniacal nitrogen were high, because some of the nitrilic compounds hydrolyzed to ammonia during distillation. A quantitative method for determining the distribution of nitrogen in the reaction products between ammoniacal and nonammoniacal forms was not available.

Reaction of Phosphorus, Dry Air, and Ammonia. The reaction between ammonia gas and phosphoric oxide vapor to form solid products is exothermic. The heat of reaction raised the temperature in the reaction chamber by about 60° C. From the results of a separate test, the heat of reaction was calculated to be about 188 cal. per gram of phosphorus. The heat of combustion of

phosphorus vapor is about 5760 cal. per gram of phosphorus.

The reaction between ammonia and phosphoric oxide was incomplete (unreacted P₄O₁₀ was in the product) when the reaction temperature was below about 230° C. When it was in the range of 250° to 350° C., the reaction proceeded smoothly and essentially to completion. Some glassy, low-nitrogen material was formed in all these tests, and the proportion of glassy material tended to increase with an increase in the temperature; when the reaction temperature exceeded 350° C., it increased rapidly with an increase in temperature. The optimum reaction temperature probably is about 315° C. The thermal stabilities of products of the reaction of phosphorus, air, and ammonia will be discussed subsequently.

An input mole ratio of nitrogen to phosphorus of about 1.25 was required to yield a product containing a N:P mole ratio of about 1.0 (range of 0.98 to 1.08). Lower input ratios gave products that were deficient in nitrogen, and they probably contained unreacted phosphoric oxide. Input N:P mole ratios greater than about 1.25 had no significant effect on the N:P ratio of the reaction product.

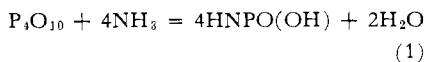
Table I summarizes the results of tests when phosphorus vapor was burned

with dry air and the resulting phosphoric oxide was reacted with ammonia.

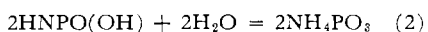
The products obtained were white powders of low bulk density. Those with N:P mole ratios of 0.98 to 1.08 did not become moist or cake when exposed to the laboratory atmosphere. Substantially all the input phosphorus was recovered in the reaction products. That part of the input ammonia not found in the reaction products was recovered as unchanged ammonia by scrubbing the effluent gas with standard sulfuric acid.

Attempts to identify the chemical compounds in the reaction products were unsuccessful. Qualitative tests, however, showed the presence of metaphosphate. Metallic salts precipitated from water solutions of the products contained both phosphorus and nitrogen, but the precipitates were of variable composition. In a further attempt to identify the phosphorus-nitrogen compounds (other than ammonium metaphosphate) present in the reaction products, a sample was suspended in *sym*-tetrachloroethane and refluxed for 16 hours. The solid residue was filtered off, and the *sym*-tetrachloroethane was evaporated from the solution phase under reduced pressure at 86° C. An optical study showed that the residue contained phosphonitrilic chloride. When the tetrameric form of phosphoronitridic acid, made by hydrolyzing tetrameric phosphonitrilic chloride, was treated similarly with *sym*-tetrachloroethane, crystalline phosphonitrilic chloride was obtained. The preparation of phosphonitrilic chloride from phosphoronitridic acid or its salts does not appear to have been reported in the literature. The above results however, are believed to be substantial evidence that phosphoronitridic acid, and possibly its ammonium salt, are formed by the reaction of phosphorus, dry air, and ammonia. The reactions illustrated by the following equations, therefore, are postulated. For convenience, the monomeric form of phosphoronitridic acid is used in the equations.

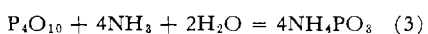
The initial reaction assumed to take place between phosphoric oxide and ammonia is



The water formed may react with half of the phosphoronitridic acid to form ammonium metaphosphate,

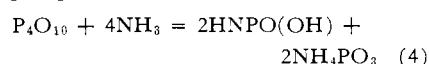


If sufficient excess water is present, all the phosphoronitridic acid might be hydrolyzed to ammonium metaphosphate and the over-all reaction would be

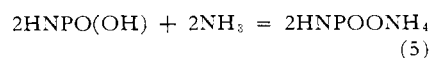


The sum of Equations 1 and 2 illustrates the over-all reaction when the N:P

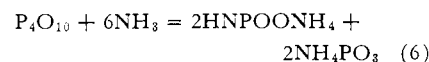
mole ratio of the reactants is 1 and phosphorus is burned with dry air



If excess ammonia is present and other conditions, such as the temperature, are favorable, the phosphoronitridic acid in the product may react further to form an ammonium salt



Because phosphoronitridic acid (monomer) is monobasic, the monoammonium salt only can be formed. Finally, Equations 4 and 5 may be combined as



The theoretical compositions of the products of Equations 3, 4, and 6 are shown in Table II, with the compositions of typical products obtained with dry combustion air under satisfactory operating conditions. The high phosphorus contents indicate that the products contain phosphoronitridic acid or its ammonium salt and, perhaps, small amounts of metaphosphoric acid or unreacted phosphoric oxide.

If the assumptions discussed above relative to the reaction between phosphoric oxide and ammonia are valid, at least half of the nitrogen in the products would be in the ammoniacal form, Equation 4. Experimental results already given are in accord with this view. Also, the maximum N:P mole ratio obtainable would be 1.5. The latter view was tested experimentally.

Reaction products from several preparations were composited and samples were treated with gaseous ammonia under atmospheric pressure at room temperatures and at 100° C. for intervals varying from 0.25 to 4 hours (Table III). The maximum N:P mole ratio in the final products was 1.54.

In another test, a reaction product that contained an N:P mole ratio of about 1.0 absorbed ammonia at 200° C. The ammoniated product had an N:P mole ratio of about 1.21. Another product with an N:P mole ratio of 1.24 was heated at 210° C. for 6 hours in a stream of ammonia without effecting a change in the N:P ratio.

The above results agree with the assumption being tested.

Physical Properties of Reaction Products

The principal product obtained by the reaction of phosphorus, dry air, and ammonia was a fluffy white powder, the finer portions of which settled very slowly from the effluent gas stream. The bulk density of the freshly prepared powdery material was between 20 and 30 pounds

Material	From Equation	Composition, %			Mole Ratio	
		P	N		N:P	NH ₃ -N: tot. N
HNPO(OH) + NH ₄ PO ₃	4	35.2	15.9	8.0	1.00	0.50
HNPOONH ₄ + NH ₄ PO ₃	6	32.1	21.8	14.5	1.50	0.67
NH ₄ PO ₃	3	32.0	14.4	14.4	1.00	1.00
Exptl. products (range)		{ 35.0	16.5	12.0	1.05	0.70
		{ 34.8	18.6	12.7	1.18	0.68

Table III. Absorption of Ammonia by Reaction Product
(Five-gram samples of composited products treated with gaseous ammonia at atmospheric pressure)

Temp., ° C.	Time, Hr.	Ammonia, Gram		Composition of Ammoniated Product, %			Mole Ratio N:P
		Charged	Absorbed ^a	P	Total	NH ₃	
		Original material		35.8	16.5	11.6	1.02
25 ^b	0.25	0.75	0.30	32.2	19.4	14.8	1.33
	0.5	0.75	0.31	33.4	21.7	14.6	1.44
	1.0	0.75	0.36	33.6	20.8	14.7	1.37
	2.0	0.75	0.36	32.2	20.7	15.5	1.42
	4.0	0.75	0.37	32.2	21.5	17.8	1.48
	1.0	1.50	0.37	33.6	21.7	15.7	1.43
100	2.0	0.38	0.32	32.4	20.0	14.7	1.36
	3.0	0.57	0.39	32.0	20.5	14.1	1.42
	2.0	0.62	0.44	31.0	21.4	16.0	1.53
	0.25	0.75	0.28	33.2	19.8	14.7	1.32
	0.5	0.75	0.33	32.2	20.5	15.4	1.41
	1.0	0.75	0.37	34.2	21.0	15.4	1.36
	2.0	0.75	0.33	32.6	21.4	15.5	1.45
	4.0	0.75	0.45	30.4	21.2	16.2	1.54
	0.5	1.50	0.28	31.4	19.4	15.5	1.36
	1.0	3.0	0.30	33.6	20.3	15.5	1.34
	2.0	6.0	0.35	33.6	20.7	16.0	1.36

^a Increase in weight.

^b Initial temperature; heat of reaction increased temperature to as high as 57° C.

Table IV. Hygroscopicity of Reaction Products, Room Conditions

Sample ^a	Days				
	30	60	90	120	230
	Weight Gain, %				
7-P	7.6	6.8	13.5	14.2	13.0
7-D	13.2	13.0	20.2	21.3	20.1
8-P	6.4	4.8	19.4	22.1	20.2
8-D	14.5	14.3	9.8	12.5	10.4
9-P	6.3	4.7	10.4	10.8	10.6
9-D	12.1	10.6	14.7	16.7	16.2
10-P	14.0	15.0	22.0 ^b	23.0	21.3
10-D	14.0	15.0	21.1	21.9	20.1
11-P	12.7	12.7	19.3	20.9	19.4
11-D	15.9	15.9	22.7 ^b	23.7	22.3
12-P	16.0	16.4	22.9 ^b	24.1	22.8
12-D	19.3	19.5	24.0 ^b	25.7	23.6

^a P, from electrostatic precipitator. D, from baffled collector.

^b Samples caked after 90 days' storage, but not moist during test period.

per cubic foot. On standing for several days in a closed container, it settled to a bulk density of about 50 pounds per cubic foot.

The tendency of a fertilizer material to absorb moisture from the atmosphere and to become wet while handling or to cake in storage, is undesirable. This property is called hygroscopicity in the fertilizer trade. Several of the products of reaction of phosphorus, air, and ammonia were subjected to hygroscopicity tests. In one set of tests samples of the powdery reaction products were stored

for 230 days (February to October) in unsealed single-walled paper bags in a room in which the air was not conditioned. The temperature of the room varied from 21° to 38° C., the relative humidity from about 35 to near 100%. The gain in weight (assumed to be absorbed water) was determined several times during the storage period (Table IV).

All samples gained weight (ranging from about 11 to 26%) during the first 120 days of storage, but then lost weight between the 120- and 230-day weighings

as the air became drier during the fall. One third of the samples were caked after 90 days' storage, but were not moist. None of the other samples caked or became moist during the test period.

In another set of tests, samples of reaction product were exposed at 25° C. for 15 hours to air having a relative humidity of 65%. The pertinent data (Table V), show that the test materials gained in weight from 2.6 to 24.4%. However, only two of the 38 samples tested were wet at the end of the test period.

A sample of pure tetrameric phosphorotridic acid treated in the same way gained about 1.6% in weight and remained free-flowing. When this material was exposed for 45 minutes at 30° C. and a relative humidity of 80%, it gained 1.7% and remained free-flowing.

These results show that materials having a relatively low hygroscopicity, which may meet the requirements of fertilizers, can be prepared by the reaction of phosphorus, air, and ammonia. Tetrameric phosphorotridic acid is nonhygroscopic.

Thermal Stability of Reaction Products

To measure the effects of the temperature in the reaction zone and the ratio of the reactants, a study was made of reaction products when they were heated at different temperatures in an atmosphere that contained varying amounts of ammonia.

Reaction products prepared in the laboratory, when heated at 300° C. in a stream of dry air, lost ammonia slowly. Between 75 and 85% of their total nitrogen was evolved on heating at 400° C. for a few hours.

Tests were made also with reaction products that were prepared at different temperatures in a pilot plant (9). These tests were made in an apparatus in which a weighed sample of material in a porous thimble (fused alumina) was suspended in a vertical glass tube surrounded by a tube furnace. The temperature of the furnace was controlled automatically by a recorder-controller activated by a thermocouple positioned in the annular space between the glass tube and the furnace wall at the elevation of the suspended sample.

A mixture of metered quantities of nitrogen and ammonia was passed upward through the glass tube. The effluent gas was analyzed for ammonia by absorbing the ammonia in standard sulfuric acid. The rate and extent of decomposition of the test materials were found from the incremental and total amounts of ammonia evolved; the maximum partial pressure of ammonia was calculated from the incremental analyses of the effluent gas.

In one set of experiments, samples of the test materials were heated at 382° or 538° C. and at 58 or 105 mm. imposed partial pressure of ammonia. The heating was continued until the evolution of ammonia was slow. The results of a typical test, showing the rate of evolution of ammonia as a function of the time of heating, are plotted in Figure 2. In another set of experiments, samples of the test materials were heated in several successive steps at 260° to 538° C. under an imposed partial pressure of 105 mm. of ammonia. Both the rate and extent of decomposition were determined for each temperature by measuring the ammonia liberated. The decomposition at each temperature began rapidly, reached a maximum, and then decreased rapidly. Except at 260° and 330° C., decomposition at a measurable rate continued 45 minutes, and the temperature was increased to the next stage before decomposition ceased. The results of a typical experiment are plotted in Figure 3. The N:P mole ratio in the residue after each heating step, calculated from the mole ratio of the initial material and the ammonia liberated, is shown also in Figure 3.

Other data from these experiments showed that products containing N:P mole ratios greater than 1.0 lost ammonia when heated at 260° C. and above; products with a mole ratio of 1.0 were unstable at 370° C.; all the test materials fused when heated at 400° C. and on prolonged heating at 538° C. lost essentially all their nitrogen; partial pressures of ammonia of 58 or 105 mm. had no significant effect on the degree of decomposition of the test materials when they were heated in the range 260° to 538° C.

The adequacy of the method of determining the degree of decomposition as described above was checked by analyzing the residues from samples that were heated at three temperature levels, 370°, 400°, and 510° C. The N:P mole ratios in these residues agreed with the

ratios calculated from the recovered ammonia.

These results indicate that to make

Table V. Hygroscopicity of Reaction Products in Air of 65% Relative Humidity at 25° C.

Sample ^a	Wt. Gain, %	Sample ^a	Wt. Gain, %
17-P	12.6	25-P	9.0
17-C	13.2	25-C	8.0
17-D	13.4	25-D	11.6
18-P	13.2	23-P	12.1
18-C	12.4	23-C	10.6
18-D	13.6	23-D	13.1
19-P	9.2	10-P	8.9
19-D	10.5	10-D	9.1
34-P	6.1	11-P	9.6
34-C	14.0	11-D	9.8
34-D	3.6	12-P	9.7
16-P	9.2	12-D	9.1
16-C	3.3	13-C ^b	11.0
16-D	10.4	14-P	10.2
29-P	6.7	14-C ^b	14.0
29-C	2.6	14-D	11.4
29-D	10.4	15-P	9.6
30-P	10.4	15-C	5.9
30-C	24.4	15-D	10.6

^a P, from electrostatic precipitator. C, from combustion chamber. D, from settling chamber.

^b Samples wet at end of test period.

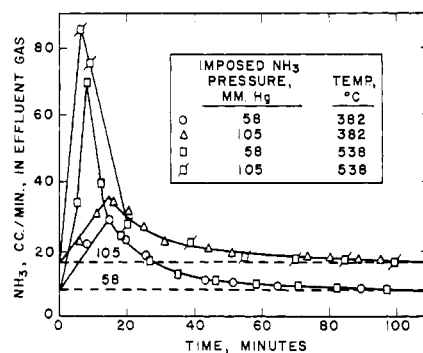


Figure 2. Decomposition of pilot-plant reaction product

Mole ratio N:P, 1.11 in atmosphere containing ammonia
 — NH₃ in input gas
 Nos., Imposed NH₃ pressure, mm. Hg

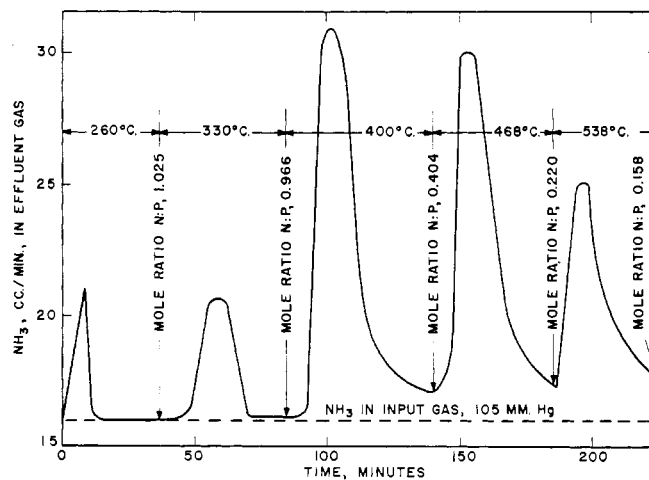


Figure 3. Decomposition of pilot-plant reaction product

Mole ratio N:P, 1.09

products containing a N:P mole ratio of 1.0 or greater, the temperature of the ammoniation step must be well below 370° C. The ammonium salt of phosphoronitric acid probably is not stable in air above about 260° C. Further, ammonium metaphosphate apparently is not stable in air at 400° C., and it decomposes almost completely on prolonged heating in an atmosphere of ammonia at 538° C.

Reaction of Phosphorus, Air, Ammonia, and Water

If the reaction illustrated by Equation 2 takes place, it is assumed that water not derived from the reaction between phosphoric oxide and ammonia (Equation 1) would react with additional phosphoronitric acid to form more ammonium metaphosphate. Ross, Merz, and Carothers (8) and Klugh (5) indicated that the reaction of phosphoric oxide, ammonia, and steam would yield, depending on the proportion of water present, ammonium metaphosphate, diammonium pyrophosphate, or monoammonium orthophosphate as the principal products. Rice (6, 7) patented a process for the manufacture of ammonium phosphate that involved reacting the fume of burning phosphorus with ammonia and steam. The chemical reactions taking place were not defined, but Rice claimed that his product had a composition, determined by chemical analysis, corresponding to ammonium metaphosphate. Also, it had a definite x-ray diffraction pattern characteristic of a crystalline chemical compound.

The effect of added water vapor on the distribution and composition of the reaction products was investigated. The input H₂O:P mole ratio was varied from 0.0 to 1.0. In these tests the input O:P mole ratio was 10, and the input N:P mole ratio was either 1.25 or 1.30. The temperature in the reaction chamber varied from 320° to 350° C., which is within the range suitable for carrying out the ammoniation reaction in the absence of added water. The results, (Table VI), show that the N:P mole ratio in the powdery products was not affected significantly by the addition of water. Both the phosphorus and nitrogen contents of the powdery products were decreased, although not in proportion to the amount of water added. The fraction of the nitrogen in the ammoniacal form increased, but not in proportion to the amount of water added. In no case was the product completely hydrolyzed to an ammonium salt of meta-, pyro-, or orthophosphoric acid, although an H₂O:P mole ratio of 0.5 is sufficient to convert all of the products to ammonium metaphosphate (Equation 3). An H₂O:P mole ratio of 1.0, the highest ratio used in these

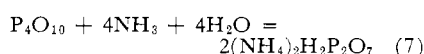
Table VI. Reaction of Phosphorus Vapor, Air, Steam, and Ammonia

Input Mole Ratio H ₂ O:P	Composition of Powdery Product						Fraction of Input P in Powdery Portion of Product, %
	P, %	N, %		Mole Ratio			
		Total	NH ₃	Tot. N:P	NH ₃ :N: tot. N		
0.0	36.3	17.1	12.1	1.04	0.71	96	
0.15	35.7	15.8	12.8	0.99	0.77	86	
0.15	35.3	15.4	12.6	0.97	0.82	90	
0.45	33.8	14.9	13.7	0.98	0.92	81	
0.45	34.3	15.5	14.1	1.00	0.91	85	
0.85	32.3	15.1	13.7	1.02	0.90	89	
1.00	35.3	15.4	13.4	0.97	0.87	82	

Table VII. Hydrolysis of Reaction Product of Phosphorus, Air, and Ammonia

HCl Added, Gram/Liter	pH of Initial Solution	Ammoniacal Nitrogen Content, Gram/Liter, of Solution after Indicated Time, Hr.				
		18	90	138	192	258
None	6.5	0.532	0.546	0.546	0.560	0.602
0.05	5.7	0.532	0.602	0.600	0.600	0.634
0.50	1.8	0.595	0.620	0.644	0.665	0.704

tests, is sufficient to form ammonium pyrophosphate



However, the fraction of the input phosphorus recovered as powdery products decreased significantly when water was added to the system. The nonpowdery, or fused products, had low nitrogen contents and probably were composed largely of metaphosphoric acid. The free water in the system, therefore, may be involved in two or more reactions.

Fertilizer Evaluation of Reaction Product

The product was completely soluble in water. In its further characterization for fertilizer use, its rate of hydrolysis was investigated as a function of pH. Four grams of a reaction product that contained 34.8% phosphorus, 19.6% total nitrogen, and 14.1% ammoniacal nitrogen were dissolved in water to make 1 liter of solution. Portions of this solution, straight and acidified with hydrochloric acid (0.05 and 0.5 gram per liter), were stored at 26° C. The content of ammoniacal nitrogen at intervals (Table VII) was a measure of the rate of hydrolysis. The results show that the hydrolysis is slow in water at room temperature. The hydrolysis is accelerated by an increase in hydrogen ion concentration, and this property of the reaction products may affect their fertilizer value.

A number of reaction products and derivatives were subjected to plant-culture tests in the greenhouse. In general, the plant-growth responses to the phosphorus and nitrogen contents of these materials were about the same as the responses to equivalent amounts of phosphorus and nitrogen in mixtures of

concentrated superphosphate and ammonium nitrate. Results from second and third crops showed that better residual effects were obtained with the reaction products than with the reference fertilizer material.

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