

NITROGEN-PHOSPHORUS COMPOUNDS PRODUCED FROM THE
VAPOR-PHASE REACTION OF AMMONIA AND PHOSPHORUS PENTOXIDE

by

ALLAN H. MACDONALD

B. S., Northeastern University, 1959

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1961

LD
2668
T4
1961.
M32
c.2

TABLE OF CONTENTS

Documents

INTRODUCTION 1

LITERATURE SURVEY 2

MATERIALS AND METHODS 11

 Materials 11

 Equipment 12

 Experimental Methods 22

 Analysis 27

PRESENTATION AND DISCUSSION OF RESULTS 32

CONCLUSIONS 56

ACKNOWLEDGMENTS 58

LITERATURE CITED 59

APPENDIX 61

INTRODUCTION

It has been the practice of the fertilizer industry to produce fertilizers of the highest possible plant nutrient content. Examples of this type of fertilizer are the ammonium phosphates. In the past, production of ammonium phosphates has been carried out by reactions between ammonia and phosphoric acid. In one such process ammonia was reacted with a phosphoric acid solution (50% P_2O_5) until all of the acid was converted to monoammonium orthophosphate with some conversion to the diammonium form. The resulting mass became solid upon cooling but retained about 20 percent moisture which is removed by drying.

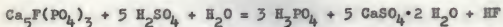
Getsinger, Houston and Achorn (8) described a more modern process for the production of diammonium orthophosphate. Phosphoric acid (78% P_2O_5) and anhydrous ammonia gas were fed to a continuous vacuum crystallizer maintained at $125^{\circ}F$ and pH of 6.5. Diammonium phosphate precipitated from the solution. The crystalline diammonium phosphate was centrifuged and dried.

Both of the described processes required heavy processing equipment and both used phosphoric acid. The two common processes employed in the production of phosphoric acid - the wet-process and the furnace process - require heavy processing equipment. The furnace process produces elemental phosphorus from phosphate rock in either electric or blast furnaces. The reaction

$$2 (CaF)Ca_4(PO_4)_3 + 9 SiO_2 + 15 C = CaF_2 + 9 CaO \cdot SiO_2 + 6 P + 15 CO$$

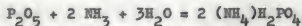
describes the process. The phosphorus produced is either condensed or oxidized in an air stream to P_2O_5 . The P_2O_5 is absorbed in towers in a water spray to form phosphoric acid.

The wet-process method of producing phosphoric acid may be described by the reaction



The process required a series of tanks to contact the phosphate rock with the sulfuric acid. The calcium phosphate was separated by filtration and the phosphoric acid was concentrated by evaporation.

More recently investigations on a research and development scale have been conducted on processes for producing concentrated fertilizer materials by the vapor phase reaction of P_2O_5 , NH_3 , and water vapor. An equation of the type



was first assumed to describe such a reaction. However, the reaction was found to be more complex in nature. A process which used a reaction of this type would produce concentrated fertilizer material without the large investment and high operating costs associated with present wet-process methods of production.

With the above factors in mind, this investigation was undertaken. The equipment was of small-scale pilot plant size. Studies were conducted on process variables and methods of collecting the reaction products.

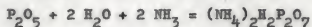
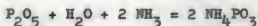
LITERATURE SURVEY

The first Americans to experiment with the vapor phase reactions between ammonia, phosphorus pentoxide, and water vapor were Ross, Merz and Carothers (14) in 1916. They proposed a process for obtaining a dry concentrated fertilizer material without the use of the heavy equipment

necessary in wet-process production. In their patent, they proposed a modification of the furnace method of preparing phosphoric acid. They proposed to contact the P_2O_5 fume coming from the furnaces with ammonia and water vapor. The gases, upon cooling, reacted through the medium of the water vapor present to form a compound--

Such as ammonium metaphosphate, ammonium pyrophosphate, ammonium orthophosphate, or other compound of a phosphorus oxid and ammonia with water. Which particular compound will be formed will depend upon conditions, as, the amount of water vapor present, the temperature of the reacting gases, and the like.

They offered the following chemical equations to represent the possible reactions:

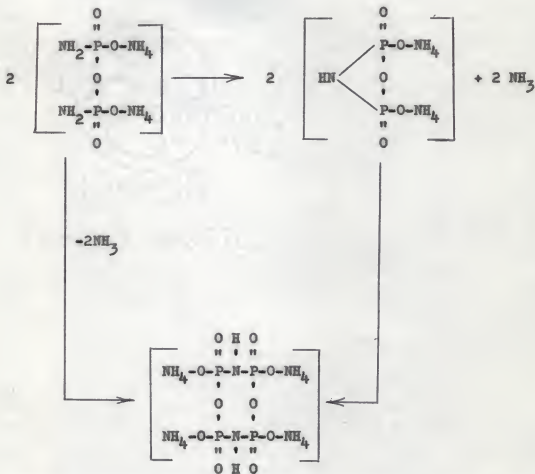


Woodstock (20) reacted anhydrous ammonia with solid P_2O_5 to form a water softening material. He reacted anhydrous liquid or gaseous ammonia with P_2O_5 at a temperature well below $150^{\circ}C$ and then heated the products of the initial reaction at a temperature above $150^{\circ}C$ for one to three hours. Woodstock stated that the products obtained from the initial reaction had very little calcium ion holding power. Calcium ion repression is a necessary property of water softeners. Upon heating at $150^{\circ}C$ and above, further reaction occurred from which a compound of high calcium ion repressing power was obtained. The products contained nitrogen in ammoniacal and non-ammoniacal form.

Woodstock presented essentially two methods of reacting the NH_3 and P_2O_5 . The first was to contact a vigorously agitated bed of solid P_2O_5 with either liquid or gaseous ammonia. The second method was to

suspend the P_2O_5 in an inert liquid medium such as a paraffin oil. The ammonia was then added to the P_2O_5 dispersion. The reaction products were separated from the oil by filtration.

Woodstock proposed the following three compounds as products of the initial or low temperature reaction, which are related by the equations shown:



These intermediate products had low calcium ion repressing power. When heated above 150°C , the intermediates lost ammonia and the nitrogen to phosphorus ratio decreased to 1.25 : 1 or less in the final products. Condensation and polymerization reactions were assumed to take place in the final high temperature step. The final products exhibited calcium ion repressing power comparable to sodium hexametaphosphate, a common

water softener.

Rice (13) presented a method of producing ammonium metaphosphate by the vapor-phase reaction of P_2O_5 , ammonia, and water vapor. Molten elemental phosphorus was supplied to a reactor where it was oxidized to P_2O_5 with atmospheric air containing the water vapor. The air was supplied in twenty to thirty times the stoichiometric amount to completely oxidize the phosphorus. The ammonia could be introduced with the air or fed into the system downstream from the phosphorus inlet. The ammonia to phosphorus feed ratios varied from 1.25 : 1 to 2:1 on a weight basis. Rice stated that the reaction was vapor phase above $600^{\circ}F$ and that below $600^{\circ}F$ a phosphoric acid was formed. Ammonia begins to dissociate to N_2 and H_2 at about $900^{\circ}F$ and therefore the reaction temperature should be below $900^{\circ}F$. Rice found that the product decomposed to a sticky, hygroscopic substance glassy or amorphous in nature if the reaction products were not rapidly cooled. Cooling of the products to $400 - 450^{\circ}F$ in less than eight seconds resulted in a dry microcrystalline product which Rice called ammonium metaphosphate. He suggested that the cooling be accomplished by a large excess of air, a large excess of air with a water spray or quench, or excess air and a heat exchanger.

Christian (3) proposed a two-stage process for reacting phosphorus and ammonia. He heated elemental phosphorus to $130^{\circ}C$ and passed a gaseous mixture of oxygen, ammonia, and some inert gas such as nitrogen or argon over the molten phosphorus. The gas mixtures ranged from 10-15 percent NH_3 , 1-2 percent O_2 and 83-89 percent N_2 . The reaction products passed directly to a heating zone where they were heat-treated at $485-600^{\circ}C$ for 0.2 to 1.0 seconds. The heat-treated product, termed an

intermediate, was collected in an electrostatic precipitator or other suitable collection device. The second stage of the process consisted of treating the intermediate in an autoclave with liquid anhydrous ammonia. Five to ten pounds of ammonia were used per pound of intermediate. The temperature ranged from 100 to 300°C and the pressure from 120 to 500 psig. The processing time in the second stage ranged between 1 and 20 hours depending upon the temperature of the operation. The product in its final form was a grey, finely divided, amorphous solid which contained 28-30 percent nitrogen and 28-30 percent phosphorus on a weight basis.

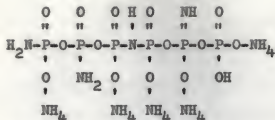
Christian (4) also patented a similar process using the same technique. In this case he used a gas mixture of 10-15 percent NH_3 , 1-1.5 percent O_2 and 83.5-89 percent N_2 . The reaction products were collected without heat-treating or further processing. The product analyzed as an amidophosphoric acid containing 19 percent nitrogen and 30 percent phosphorus. Christian also stated that previous attempts to react phosphorus, ammonia, and oxygen had resulted in "hygroscopic, semi-pyrophoric, or noxious smelling materials which were difficult to handle and unsatisfactory for most of their anticipated uses". Christian claimed that more than 5 percent O_2 in the gas mixture resulted in a semi-pyrophoric product.

Two large organizations connected with heavy-chemicals production have experimented with the reaction between P_2O_5 vapor and ammonia. Monsanto Chemical Company is the first of these. Monsanto has two patents (11) and (12) on a process for the vapor phase reaction between P_2O_5 , NH_3 , and H_2O . Van Wazer (17) summarized the results of Monsanto's studies. Van Wazer gave the most versatile method of preparation as

reacting a controlled mixture of ammonia and water vapor with a hot stream of P_2O_5 vapors. The reaction was carried out at approximately $345^\circ C$. The hot P_2O_5 vapors were made from the burning of elemental phosphorus in the same apparatus. Almost immediately after mixing the hot P_2O_5 with the ammonia and water vapor, the gas stream was quenched and the products collected. The product, as collected, exhibited some acidic properties and was calcined at $100^\circ C$ with 100 percent by volume ammonia. The final product contained 26.05 percent nitrogen and 70.7 percent P_2O_5 . The product characteristics and composition were dependent upon (1) the NH_3 : H_2O : P_2O_5 ratio, (2) the temperature of the P_2O_5 vapor, and (3) the time interval between mixing the reactants and quenching the products.

Other methods for reacting P_2O_5 and NH_3 are discussed in a British Patent issued to Monsanto Chemical Company (12). These remarks seemed directed at the work by Woodstock previously described. They conclude that reactions between NH_3 and solid P_2O_5 are subject to the following undesirable features. Reactions between solid P_2O_5 and NH_3 form an impervious crust on the surface of the P_2O_5 which inhibits further reaction. Reactions carried out by suspending the P_2O_5 in a solvent are undesirable because the product retains 10-20 percent of the solvent.

Van Wazer stated that the products resulting from the reaction of P_2O_5 , NH_3 , and H_2O were classed as chain phosphates with some amido and imido groups. Assuming that no P-P bonds were formed, that all of the phosphorus was quadruply connected, and that no rings form, Van Wazer presented the following structural formula for the reaction products



Van Wazer also presented a method of classifying and naming phosphates according to composition or structure. He defined M as one equivalent of any cation or organic radical. He further stated that all phosphates may be presented as $x M_2O \cdot y P_2O_5$, where M_2O may represent a mixture of different cationic oxides. By letting R equal the M_2O to P_2O_5 ratio, Van Wazer defined all phosphates in the following manner:

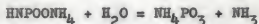
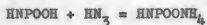
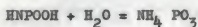
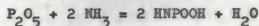
R=3	orthophosphates
R=0	P_2O_5
$1 < R < 3$	Polyphosphates. R=3 - the orthophosphates - and R=2 - the pyrophosphates - were treated as a special polyphosphates
R=1	metaphosphates
$0 < R < 1$	ultraphosphates

Phosphates in which $R > 3$ were defined as mixed salts as the charge on a single PO_4 group can not balance more than three equivalents of cation.

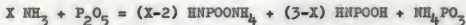
The second large organization to study the reaction of P_2O_5 and NH_3 was the Tennessee Valley Authority. TVA has published more information than any other single investigator or organization.

Driskell, et. al. (5) and Driskell (6) stated that any water vapor present reacted with some P_2O_5 to form metaphosphoric acid polymer which collected in the reaction zone in the form of a viscous, glassy material. Driskell therefore proposed a process whereby phosphorus vapor was burned with previously dried air. The P_2O_5 from the combustion was

contacted with anhydrous NH_3 at any point where the temperature was between 550 and 700°F. The dry, white, powdery reaction product was collected in an electrostatic precipitator. Driskell proposed the following reactions as taking place to form the product, which was a mixture of phosphoronitridic acid (HNPOOH), ammonium phosphoronitridate (HNPOONH_4), and ammonium metaphosphate (NH_4PO_3):



He then proposed the following equation to describe the overall reaction:



where X is a number between 2 and 3. The mixed products were analyzed and found to contain 32.5-34.0 percent phosphorus and 16-18 percent nitrogen with 65-85 percent of the nitrogen existing in ammoniacal form.

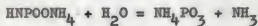
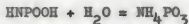
Stinson, et. al. (16) described a similar reaction with water vapor present in the system. The same equations were presented to describe the reactions occurring. The products when water vapor was present were analyzed to contain 13-16 percent nitrogen and 70.5 percent P_2O_5 . Eighty-nine percent of the nitrogen was in ammoniacal form. Stinson briefly described the analytical procedures used to confirm the presence of phosphoronitridic compounds.

In comparing the data presented by Driskell and Stinson the main differences in the reaction products obtained was the percentage of ammonium metaphosphate in the product. Driskell reported that 70 percent of the product was NH_4PO_3 when no water vapor was present in the

system. With water vapor present, Stinson reported the products to be 89 percent NH_4PO_3 . In both instances the products were dry powdery materials with an approximate bulk density of 15 pounds per cubic foot.

The products exhibited two characteristics which were undesirable in fertilizers. The first was the low bulk density which would create storage, shipping, and handling problems. The second undesirable property was the fact that the products were hygroscopic.

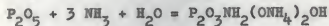
Hignett, et. al. (9) and Stinson, et. al. (16) described a process where the above mentioned reaction products, now termed intermediates, were calcined with steam at 250°F to produce a less hygroscopic and more dense product. The bulk density increased from 15 to 45 pounds per cubic foot. The process was accompanied by ammonia losses. The following reactions were proposed:



The products from this treatment contained 14.5 percent nitrogen and 73 percent P_2O_5 . Approximately 95 percent of the nitrogen was in ammoniacal form. From analysis of the process and reactions, Hignett deduced that the hygroscopicity of the intermediates was primarily due to the presence of HNPOOH.

Greenhouse tests conducted on the mixed reaction products (5) indicated that about the same response was obtained as from a reference material. Second and third crops showed better residual effects from the mixed reaction products than from the reference fertilizer. The reference fertilizer was a mixture of superphosphate and ammonium nitrate prepared to have amounts of nitrogen and phosphorus equivalent to the mixed reaction products.

Driskell (6) also summarized the work of Sanfourche in Europe. Sanfourche burned red phosphorus in a mixture of air and nitrogen and added ammonia to the combustion products. He postulated the reaction product to be diammonium amidopyrophosphate formed by the reaction



Sanfourche investigated the effects of moisture on the reaction and found that the yields decreased when moisture was not present in the system.

Wang (18) conducted the initial experimental studies here at Kansas State University and constructed the basic equipment used for these studies. Wang used an electrostatic precipitator to collect the products. Attempts to collect the products using filters and cyclone collectors proved ineffective. His studies indicated that a NH_3/P_2O_5 molar feed ratio of 6.6 represented the minimum desirable feed ratio. The addition of water vapor to the system did not seem to contribute to the reaction or change the composition of the products. This may have been due to the fact that the compressed air used was not dry and sufficient water vapor may have entered the system in the air to make the addition of water unnecessary. Wang also found that the reaction products exhibited calcium ion repressing power and would therefore be useful as water softeners.

MATERIALS AND METHODS

Materials

The materials used in this study were air, anhydrous ammonia, and

elemental phosphorus. The air was obtained from the compressed air lines present in the building. The ammonia was refrigeration grade from the Spencer Chemical Company and was contained in a conventional gas cylinder containing 100 pounds of gas. The cylinder was fitted with a pressure regulator. The phosphorus was purchased from Fisher Scientific Company in one pound or eleven pound lots. It conformed to National Formulary specifications for white phosphorus. Due to its low flame temperature (34°C), the phosphorus was stored under water. Great care was exercised when handling the phosphorus as it is poisonous as well as a fire hazard. Transfers of phosphorus from storage to the apparatus were made while wearing rubber gloves and safety goggles. The phosphorus was handled with tongs.

The reaction products as initially collected were too light and too finely divided to be used in the fluidized beds. Therefore these products were compressed in a die with a Carver Laboratory Press. The compressed pellets were crushed and the desired particle size separated by screening. Plate I shows the product in its three forms.

Equipment

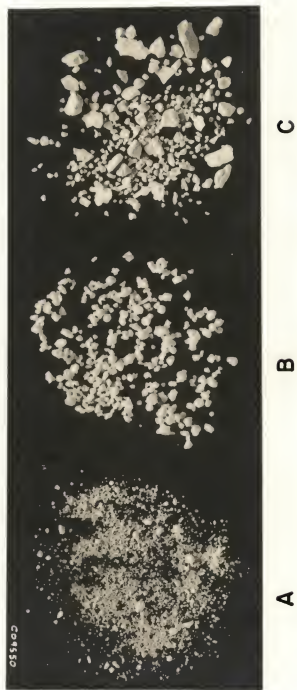
Plate II shows the reactor and associated equipment used in this study. The reactor was a 2-inch stainless steel pipe. The combustion and reaction were carried out in this piece of pipe. In further discussion in this paper the terms "combustion zone" and "reaction zone" are used. The combustion zone is defined as the section of pipe between the phosphorus and ammonia inlets. The reaction zone is defined as the section of pipe downstream from the ammonia inlet. The

EXPLANATION OF PLATE I

Various Forms of the Product

- A. Product as obtained immediately after collection in the bag filter.
- B. Sized particles after use in fluidized bed.
- C. Compressed and crushed product before sizing and use in fluidized bed.

PLATE I

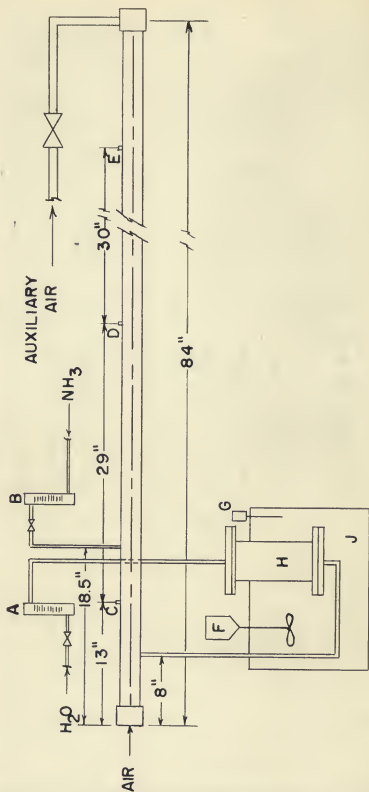


EXPLANATION OF PLATE II

Drawing of Reactor and Associated Equipment.

- A. Water flowmeter
- B. Ammonia flowmeter
- C. Thermocouple well no. 1 (T_1)
- D. Thermocouple well no. 2 (T_2)
- E. Thermocouple well no. 3 (T_3)
- F. Mixer
- G. Immersion heater
- H. Phosphorus melter
- J. Water bath

PLATE II



phosphorus melter was made of a section of 4-inch pipe with flanges at both ends. The phosphorus was fed to the system by metering water into the top of the melter and forcing molten phosphorus into the combustion zone. The ammonia flow was measured at 10 psig. The primary air flow was controlled by a globe valve and measured by an orifice plate and mercury manometer. The auxiliary air flows were not measured. The temperatures were measured by a potentiometer and iron-constantan thermocouples located at the positions shown. A 16 point Brown temperature recorder was also used in the later runs. The stainless steel reactor was connected to the collection system by 2-inch black iron pipe. The products were of a corrosive nature and the black iron pipe had to be replaced after one year's service.

The electrostatic precipitator is shown in Plate III. Actual collection took place inside the inner tube of the collector. This tube was eight inches in diameter and nine feet long. The electrons discharged from the negative electrode hanging in the center of the tube. The electrode was $5/8$ inches in diameter and nine feet seven inches long of prong and star construction. The electrode was suspended from a ball joint so that it could be centered.

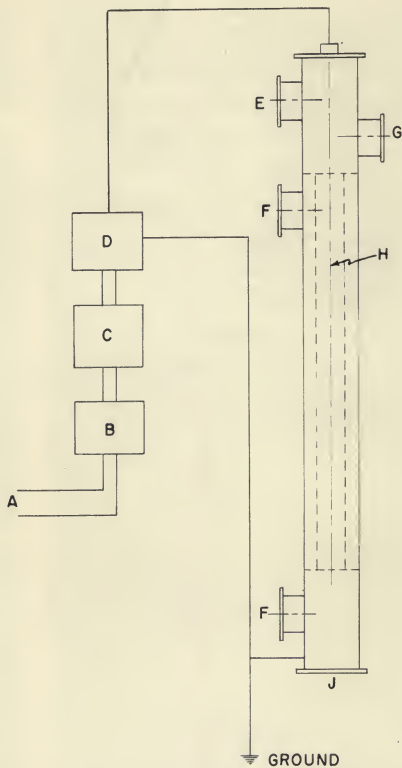
Plate IV shows the equipment arrangement for collection studies involving the bag filter and fluidized bed. The filter was made of glass cloth three feet long and $22\frac{1}{2}$ inches in diameter - open at both ends. The filter was made to fit a 55 gal. drum head. In studies involving the filter alone, the bag was mounted on a drum head and fitted in the two inch by-pass line. The top end of the bag was tied shut. The empty column was used as a by-pass in this instance. In studies involving fluidized beds and the bag filter in combination, the filter

EXPLANATION OF PLATE III

Drawing of Electrostatic Precipitator and Auxiliaries

- A. Power supply; 220 volts, 60 cycles single phase
- B. Control cabinet
- C. High voltage transformer
- D. Rectifier
- E. Hand hole
- F. Gas inlets
- G. Gas outlet
- H. Emitting electrode (negative)
- I. Manhole for product removal

PLATE III

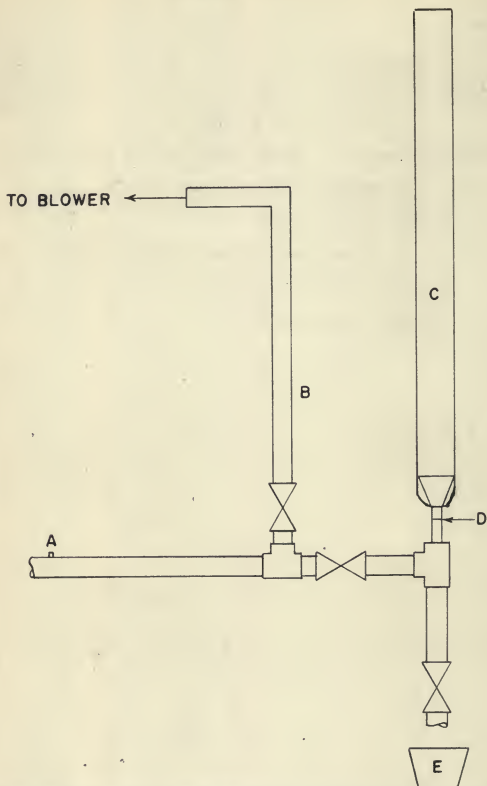


EXPLANATION OF PLATE IV

Equipment Arrangement for Fluidized Bed and Bag Filter Studies

- A. Thermocouple well no. 4 (T_4)
- B. By-pass line
- C. 4-inch pyrex column for fluidized bed
- D. Bare thermocouple (T_5)
- E. Plastic bucket

PLATE IV :



bag was tied to the top of the column. The gases and product fed through a 1-inch pipe to a pyrex glass pipe expansion where the diameter was expanded to four inches. The column placed on top of this expansion was four inches in diameter and four feet long. A four-inch by two-inch glass reducer was fixed to the top of the column. The filter bag was tied to this reducer. Plate IV also shows the locations of the fourth and fifth thermocouples. In all instances the by-pass line was connected to an exhaust blower by an eight-inch sheet metal duct.

Plate V shows the variations used with each type of fluidized bed studied. A conical sheet metal distributor, employed in both the fluidized bed and the fluidized bed with baffles, was used to make the expansion from two to four inches less abrupt. A ping-pong ball was used as a bed support in the fluidized bed experiments. The fluidized bed with a packed calming section had a packing of berl saddles and ceramic balls beneath the fluidized bed. The packing was supported on an expanded metal screen. The baffles used in studies of fluidized bed with baffles also were made of expanded metal screen. The baffles were spaced at two inch intervals up through the column.

Experimental Methods

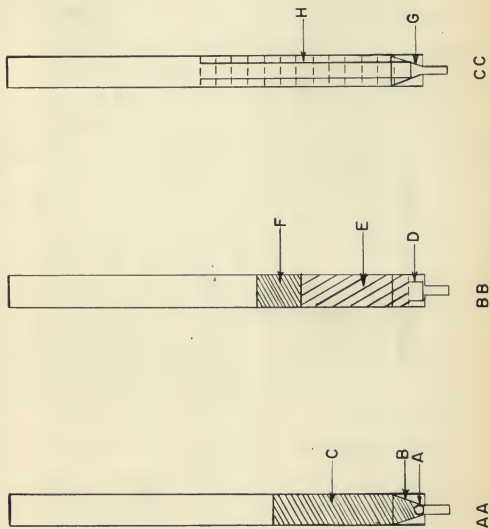
The normal operating procedure of the reactor did not vary during the entire investigation. The variations in experimental procedure occurred in the operation of the collection systems investigated. Normal reactor operation consisted of first charging the phosphorus melter with elemental phosphorus. The mixer and electric immersion heater were then started. The amount of power supplied to the heater was controlled

EXPLANATION OF PLATE V

Illustration of the Three Types of Fluidized Beds

- AA. Fluidized bed
- BB. Fluidized bed with packed calming section
- CC. Fluidized bed with baffles
- A. Ping-pong ball bed support
- B. Conical transition piece
- C. Bed of product
- D. Packing support
- E. Packed calming section
- F. Bed of product
- G. Conical transition piece
- H. Baffles

PLATE V



by a powerstat. Agitation was found necessary to maintain the water bath at a uniform temperature. The bath was heated until it reached a temperature of 55°C . The power supply was then adjusted so as to maintain this temperature throughout the rest of the run.

Once the bath reached 55°C the air flow was started. The phosphorus flow was then started at a predetermined rate. Since the flame temperature of the phosphorus (34°C) is below its melting point (45°C) combustion of the phosphorus was almost always spontaneous. However, in some instances, uneven phosphorus flow caused by cooling of the liquid phosphorus in the feed line made heating of the feed line and combustion zone by a gas flame necessary. Once the phosphorus flow became regular and the combustion smooth, the air rate was adjusted to give the desired combustion temperature. The ammonia flow was then started at the desired rate.

With the startup now completed, the flow rates were kept as constant as possible through manual control. The reaction was allowed to reach steady state temperatures before any data was taken or collection attempted. By-pass lines were used until steady state was reached. When the temperature recorder was used, the combustion was limited to temperatures below 800°F as this was the upper limit of the instrument.

When the electrostatic precipitator was used for collection, the reaction products were allowed to pass through it during the start-up as no collection was possible until the power was turned on. When the reaction had reached steady state, the power supply was turned on and the powerstat on the control panel adjusted until arcing occurred within the precipitator. Then voltage was then decreased until the arcing stopped. This condition corresponded to approximately 32,000 volts

with less than 0.1 amps of current. As the product collected, it was necessary to decrease the voltage to prevent arcing within the precipitator. After sufficient product had been collected and the data taken, the flows of phosphorus, ammonia and air were stopped in that order. The back of the precipitator control cabinet was opened activating a ground which discharged the precipitator. Before any work was done on the precipitator, safety ground lines were attached to the control cabinet and precipitator electrode. The precipitator was then opened and brushed clean of product. The product was weighed and stored in jars for analysis.

When the bag filter was used for collection, the procedure was the same except that the column was used as a by-pass until steady state was reached. At steady state the flow was switched to the bag filter. When enough product had been collected, the phosphorus and ammonia flows were stopped. The by-pass was again opened and the air flow increased to aid in cooling the reactor. The runs with the bag filter were long (1-2 hrs) and the filter was used to collect enough material to form the fluidized beds.

When the fluidized beds were used in combination with the bag filter, the procedure was similar to that for the bag filter only. The filter was tied to the top of the glass column. The 2-inch pipe by-pass line was used until steady state operation was reached. At the end of a run the phosphorus and ammonia flows were stopped and the by-pass opened. The air was again used to aid in the cooling of the reactor. When the fluidized bed alone and the fluidized bed with packed calming section were used, the beds were dumped into the column before start-up.

When the fluidized bed with baffles was used, the bed was not placed

in the column until after the operation had reached steady state and the flow of product was switched to the column. This was necessary because no bed support was used. In all cases where one of the various types of fluidized beds were employed, auxiliary air was used to acquire the desired degree of fluidization or motion in the beds. At the end of a run, the phosphorus and ammonia flows were stopped and the by-pass opened. In the cases of the fluidized bed and the fluidized bed with baffles, the bed flowed out the bottom of the column and into a plastic bucket when the by-pass was opened. When the packed calming section was used, the column had to be dismantled to recover the bed and packing.

The equipment was washed clean after each run to insure as nearly as possible that the same conditions existed inside the equipment for each run.

Analysis

Four standard tests were made on the products. These were moisture content, total nitrogen, ammoniacal nitrogen, and phosphorus pentoxide.

For the moisture determination, a 2-gram sample was weighed in a weighing bottle to four decimal places. The sample was placed in an oven maintained at 100°C for five hours ± ten minutes. The sample was removed from the oven and placed in a desiccator with the cover of the bottle in place for one hour to cool. After cooling, the sample was re-weighed to the same four decimal place accuracy. The moisture content was recorded as:

$$\frac{\text{loss in weight}}{\text{original sample weight}} \times 100 = \% \text{ moisture.}$$

The samples were analyzed for total and ammoniacal nitrogen by the Chemical Service Laboratory. The analyses were made by the standard A.O.A.C. methods (1).

The method used for determining phosphorus pentoxide was a slight revision of the colorimetric method reported by Bridger, Boylan, and Markey (2). Colorimetric analyses of this type normally obey the Lambert-Beer Law for transmittance:

$$\frac{I}{I_0} = 10^{-k c t}$$

where $\frac{I}{I_0}$ is the transmittance, k is the molecular extinction coefficient which is a function of the photoelectric cells and wave length of light used, t is the thickness of the sample cell, and c is the concentration of the sample analyzed in moles per liter. When the same photoelectric cells and wave length of light are used, the equation may be rearranged to the form:

$$c = A(2 - \log_{10} \%T)$$

where A is a constant, $\%T$ is the percent transmittance read from the instrument, and c is the concentration. In this case, the concentration is expressed as mg of P_2O_5 per 100 ml of solution. The percent P_2O_5 is calculated by the equation

$$c \times \frac{\text{dilution}}{\text{aliquot}} \times \frac{1}{\text{sample wt.} \times 10} = \% P_2O_5$$

where c is the concentration in mg of P_2O_5 per 100 ml, dilution and aliquot are both measured in milliliters and the sample weight is measured in grams. Bridger stated that the Beer-Lambert Law is not obeyed over the entire transmittance range. If, however, the test is designed to fall into a narrow range of transmittances; the Beer-Lambert Law may be applied without introducing significant error.

Wang (18) found that although the materials produced were water soluble, the results obtained from Bridger's method of analysis were low and unreliable unless the samples were digested in aqua regia. These low results were due to the fact that the molybdate color reagent only forms the color complex with orthophosphates. The variability found by Wang may have been due to the presence of chain phosphates which hydrolyzed slowly in water solutions. The procedure developed for the P_2O_5 test was as follows. A 0.1 g dry sample (weighed to four decimal places) was digested with 30 ml of nitric acid and 3-5 ml of hydrochloric acid in a 500 ml volumetric flask. The sample and acid were heated until the evolution of brown fumes ceased and the solution was colorless. This treatment converted all the phosphorus to the orthophosphate form. After digestion, the sample was cooled and the volume made up to 500 ml with distilled water. The solution was filtered and a 10 ml aliquot of the filtrate was transferred to a 100 ml volumetric flask. Twenty five ml of color reagent was added to the aliquot and the volume made up to 100 ml. Since the color reagent was slightly colored, a "blank" was prepared by diluting 25 ml of color reagent to 100 ml in a volumetric flask. The colorimeter, a Lumetron model 402E, was allowed to warm up for 30-60 minutes. The instrument was then "zeroed" with the color blank. The prepared sample was then analyzed. One hour was allowed for the color to develop before the sample was analyzed. A monochromatic filter (M420) was used in analysis. This filter gave light with a wave length of 420 milli-microns. In order to increase the precision of the aliquot measurements, a calibrated pipette and a Fischer "propipette" were used, giving an accuracy of about 0.01 ml. The color complex formed in this analysis was not stable, and a

kinetic effect was observed. The color development followed a pattern of rapid initial formation followed by a period of slow, gradual increase and then decay. The initial formation took approximately 15 minutes. The gradual increase occurred for 14 to 16 hours before decay began. This variation in color was the reason for specifying a one hour period between the addition of the color reagent and analysis. The same time interval was used when the colorimeter was calibrated. The above procedure was designed to produce transmittance readings between 15 and 35 percent for the fertilizer material studied.

Standard phosphate rock was used to calibrate the colorimeter. Standard solutions of phosphate rock were prepared in the same manner as the fertilizer material. These samples were designed to produce percent transmittance readings between 15 and 35. Calibrations of this nature involve the interchange of dependent and independent variable. In other words, the calibration is made using concentration as the independent variable with %T as the dependent variable. Once the calibration is made, the equation obtained is rearranged so that concentration becomes the dependent variable and is determined from %T, which is now treated as the independent variable. This may be done mathematically by simple algebraic manipulation. When statistical analysis is employed, this interchange may or may not be as simply done (7), (19). In order to keep the statistical analysis as simple as possible the following procedure was used. Twenty samples of standard rock, designed to give a range of transmittance readings between 15 and 35 percent for an M420 filter were prepared. One data point was taken for each concentration, and a linear regression analysis was made by treating the percent transmittance as the independent variable and the concentration

as the dependent variable directly. This resulted in obtaining the desired relationship with the least amount of statistical and mathematical manipulation. If more than one data point for each concentration had been taken, the direct interchange of variables could not have been made, and more complex equations (7) would have been required. The equations obtained from this analysis apply only when light of the same wave length and the same photoelectric cells used in the calibration are used for analysis. The instrument must be recalibrated if a different wave length light is used or if the photoelectric cells are replaced. A variation in results of one percent should be expected due to variation within the instrument itself.

Jones (10) presented a method for the differential analysis of phosphate mixtures. His procedure presented quantitative tests for hexametaphosphates, trimetaphosphates, pyrophosphates, orthophosphates, and qualitative tests for polyphosphates. The tests for ortho- and pyrophosphates were of primary interest as the presence of water vapor in the system may have been sufficient for the formation of these structural configurations. Although most of the tests described by Jones were of a quantitative nature, they were used qualitatively.

Fertilizer materials must be low in hygroscopicity. Stinson, et. al. (16) and Hignett, et. al. (9) indicated that the reaction intermediates obtained in their studies were hygroscopic and reacted with water vapor. Products produced in this study were observed to become sticky and shrink in volume after about a month of storage. For these reasons, a test for hygroscopicity and reaction with water was devised. Five samples of approximately three grams each were weighed to four decimal places in sample bottles. The samples were dried for one hour

in an oven at 105°C and cooled for one hour in a desiccator. The initial moisture content was determined and then the dry samples were placed in a constant humidity chamber. A saturated calcium chloride solution was used for humidity control. The temperature of the humidity cabinet was 150°F which gave a relative humidity of 18-20 percent. As each sample was removed from the humidity chamber, it was cooled 1 hour in a desiccator, weighed, dried one hour at 105°C , cooled one hour in a desiccator, and reweighed. Immediately after the final dry weight was taken a 0.1 gram sample was prepared for P_2O_5 analysis. The data recorded was total gain in weight, gain in dry weight, and P_2O_5 analysis after 0, 2, 4, 6, 8, and 10 days at 150°F and 18-20 percent relative humidity. The tests were repeated using a humid atmosphere of 100 percent saturation.

PRESENTATION AND DISCUSSION OF EXPERIMENTAL RESULTS

Experimental investigations were carried out in two areas. The first area of investigation was the effect of the flow ratios of the reactants on product composition. An electrostatic precipitator was used for collection purposes during these studies. The second area investigated was the appraisal of various other collection systems.

The products obtained in all studies had an average P_2O_5 content of 70 percent. The products were stored for future analysis in the case of P_2O_5 determinations. The effect of moisture on product composition was later found to be significant so that the stored products had undoubtedly changed in composition, and the effect of molal flow ratios of the reactants therefore could not be determined.

Total and ammoniacal nitrogen were determined by the Chemical Service Laboratory shortly after production. The products ranged from 12 to 17 percent total nitrogen. The results of the nitrogen analysis were subject to the same variation as the P_2O_5 analyses but not to as great an extent. The reactions taking place during storage are discussed in a later part of this section. The average values obtained for P_2O_5 and nitrogen content were approximately the same as those reported by Stinson, et. al. (16).

Certain operational problems were common to all phases of the experimental work. One of these was poor phosphorus recovery. Throughout all of the experimental work only 50 to 60 percent of the phosphorus fed to the system was recovered in the product. In rare instances the recovery was as low as 25 percent. These phosphorus losses were attributed to three causes. The first and largest contribution was the formation of red phosphorus. This form of phosphorus has a much lower vapor pressure and burns much less readily than white phosphorus. Van Wazer (17) stated that white phosphorus converts to the more stable red form when heated in a closed system at moderately high temperatures. He described the conversion as a first-order reaction rate in the temperature range 480-660°F. He also stated that nodules of red phosphorus formed in bricks of white phosphorus stored in water when the bricks were exposed to light. The white phosphorus used in these studies was transferred from the shipping containers to glass jars in 11 pound lots. This method of storage permitted light to contact the white phosphorus thereby contributing to the formation of some red phosphorus. The fact that the phosphorus in the melter was held at 55°C for several hours may have contributed to the formation of more red phosphorus. Further,

as the phosphorus was fed to the combustion zone, it passed from the melter at 55°C (131°F) to the reactor where the temperature was in the neighborhood of 700°F . The low phosphorus flow rates (4-10 grams per minute) exposed the phosphorus to elevated temperatures long enough before combustion occurred to account for considerable formation of red phosphorus. Larger scale equipment and improved phosphorus feeding probably could reduce the conversion to the red form considerably.

Visual inspection of the equipment after several runs revealed the presence of a green, glassy material, as well as the red phosphorus in the reactor tube. This green, glassy material has been called a polymeric form of metaphosphoric acid (5) formed from the reaction between P_2O_5 and water vapor and is undoubtedly a second cause of low phosphorus recovery.

The third cause was the collection of product on the interior surfaces of the apparatus. In rare instances the product collected in sufficient quantity around thermocouple wells to form plugs.

Dissolved air in the tap water available in the building resulted in the formation of air bubbles under the float of the rotameter used to meter the water into the phosphorus melter. A constant head tank was installed to eliminate these bubbles and to insure reasonably accurate control of the phosphorus flow.

External cooling of the reactor was attempted. A two foot section of pipe three feet below the ammonia inlet was cooled by a water spray. For some unknown reason, no product was collected when cooling was used. Operation of the equipment on the same day under the same flow conditions without cooling resulted in normal product collection.

Statistical methods were employed in the analysis of the data.

Linear regression analysis with accompanying t-tests applied to the slope of the least squares line were used to analyze for significant trends. All t-tests were applied at the 95 percent confidence level. The statistical methods employed were those outlined by Snedecor (15).

Fig. 1 shows the combustion temperatures corresponding to various air/P molal feed ratios. The phosphorus feed was kept constant at 0.32 gram atoms per minute in all cases. The original data for Fig. 1 is presented in Tables 1 and 2 in the appendix. Because of the formation of red phosphorus, the external mole ratios were not representative of the conditions existing within the system. Another source of variation was the effect of external air currents. Air currents moving across the external surfaces of the apparatus reduced the combustion temperature because of increased heat transfer rates. When a fan was placed where it would move air over the combustion zone of the reactor, decreases in combustion temperatures of 25-50°F were noted. The way in which the phosphorus burned must also be taken into consideration when interpreting Fig. 1. The phosphorus combustion - although usually spontaneous - was not instantaneously complete. In other words, the combustion was not complete at the point where the phosphorus entered the system but small particles of burning phosphorus were entrained in the gas stream and transported varying lengths along the apparatus. This entrainment led to locally high temperatures. The trend line shown in Fig. 1 represents the average combustion temperature obtained from a given air/P mole ratio. Large positive and negative deviations from the line indicated were expected. It is apparent that improved phosphorus combustion, which would be possible in larger equipment, should give much different results.

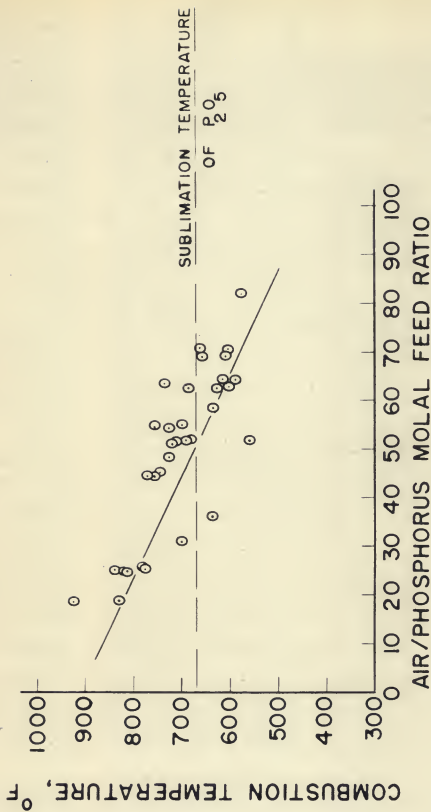


Figure 1. Relationship between air to phosphorus molal feed ratio and combustion temperature for a constant phosphorus feed rate

Fig. 2 shows typical temperature profiles obtained in these studies. Again, the air/P ratios were obtained by changing the air feed rate only. The phosphorus rate was constant at 0.32 g-atoms per min. The original data for Fig. 2 is presented in Table 2 in the appendix. The data points show the location of the thermocouples. Statistical analysis of the data available for T_3 indicated that the temperature at this location was independent of the relative air velocities used. Normally, increased air flow would be expected to decrease the temperatures due to dilution effects and increased heat transfer rates, which would normally accompany increases in air flow. Collection of the reaction products on the interior surfaces of the reactor may have provided insulation which eliminated the effects of dilution and heat transfer by the time the third thermocouple was reached.

In contrast to this, when the phosphorus flow rate was increased or decreased for a constant air rate respective increases and decreases in the entire temperature profile occurred.

In the past, the reactions of P_2O_5 and NH_3 - when carried out in apparatus where the P_2O_5 was produced by the combustion of elemental phosphorus - have been treated as vapor-phase reactions. Fig. 1 indicates, however, that the combustion temperature was not always above the sublimation temperature of P_2O_5 , depending upon the relative amounts of air and phosphorus fed to the system. Fig. 2 shows that the combustion temperature must be somewhat higher than the sublimation temperature of P_2O_5 in order for the P_2O_5 to be in the vapor state at the point where the ammonia enters the system. These two factors introduced two possible approaches to the analysis of the data. The first approach would be to consider the data to represent a single type of reaction and to

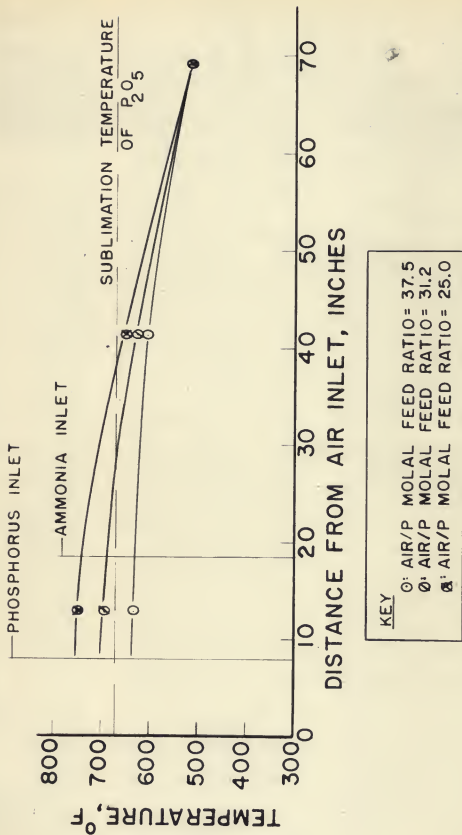


Figure 2. Temperature profiles in reactor for a constant phosphorus flow rate and variable air flow rates.

analyze the data accordingly. The second approach would be to consider two possible types of reaction, the first being a vapor-phase reaction occurring when the combustion temperature was high enough to insure the presence of P_2O_5 vapor, and the second type being a solid-vapor reaction between gaseous ammonia and finely divided, solid P_2O_5 . In actual operation it is probable that both reactions occurred in certain zones of the reactor because of the manner in which the phosphorus burned to give locally high temperatures. For purposes of classification, the data were divided into two groups using the combustion temperature as a guide. Due to the variations previously discussed, the air/P ratio of 51 could not be used to divide the data as Fig. 1 indicates. Instead, the actual temperatures observed were used, giving a dividing line between air/P ratios of 30 and 36. The group of data points with air/P ratios of 30 or less were classed as vapor-phase reactions. The data points starting with 36 and higher were classed as gas-solid reactions.

In Figs. 3 and 4, which show the effect of NH_3/P ratio on total nitrogen and percent of the total nitrogen in the ammoniacal form, the combustion temperature was above $670^{\circ}F$ for all data points and the data could not be grouped according to reaction types. The original data for Figs. 3, 4, 5 and 6 is presented in Table 1 in the appendix. Statistical analysis was not used on these data. The shapes of the two curves indicated that for NH_3/P molal feed ratios greater than 2.0 the total nitrogen content did not exceed an average of 15 percent and existed entirely in ammoniacal form. NH_3/P ratios below 2.0 resulted in a decrease in total nitrogen and the presence of other forms of nitrogen in the products. The same variations discussed for Fig. 1 were present in Figs. 3 and 4. Therefore, the molal ratios presented do not represent

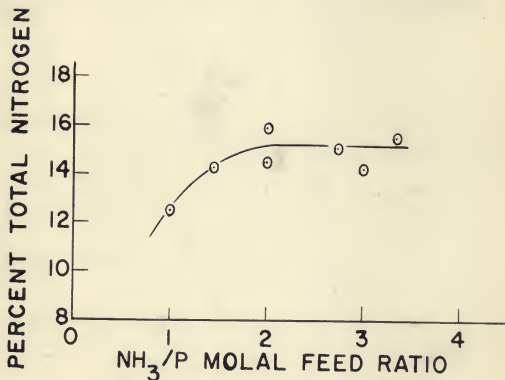


Figure 3. The effect of ammonia to phosphorus molal feed ratio on the total nitrogen content of the products for an air to phosphorus molal ratio of 25.

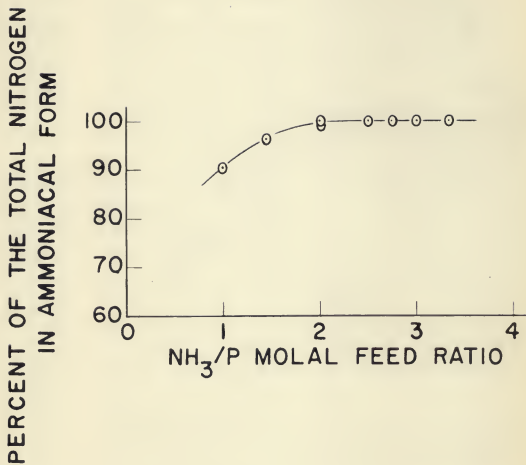


Figure 4. The effect of the ammonia to phosphorus molal feed ratio on the fraction of the total nitrogen existing in ammoniacal form for a constant air to phosphorus molal feed ratio of 25.

the actual conditions existing within the system.

Figs. 5 and 6 represent the effects of the air/P molal feed ratios on the amount and form of the nitrogen present. Both figures were analyzed from the standpoints of both a single type of reaction and two possible types of reaction. Treating the data as representing a single overall reaction, Figs. 5 and 6 indicate that the total nitrogen content of the product increased with increasing air/P ratios. The amount of nitrogen present in ammoniacal form showed a corresponding decrease with increasing air/P ratios. However, when the data were analyzed considering both solid-vapor and vapor-phase reactions, no significant trends were present. The data corresponding to a vapor-phase reaction indicated an average nitrogen content of 14.6 percent with 99 percent in ammoniacal form, regardless of flow ratios. For the data representing solid-gas types of reactions, the average total nitrogen content was 16.2 percent and only 83 percent of the total nitrogen was in ammoniacal form. Again, no significant relationship between amount and form of nitrogen and the air/P ratios could be detected.

Because of the magnitude of the variations present at all times during this study, no definite conclusions were drawn concerning the type or types of reactions taking place. Nor were any definite conclusions drawn as to the effects, if any, of the ratios of the reactants. However, there was some evidence for the fact that the two different types of reactions occurred as was hypothesized. The data shown in Fig. 6 indicates that products obtained from a vapor-phase reaction contained only ammoniacal nitrogen. This would indicate that the products of the vapor-phase reactions were ammonium phosphates. The results of the analysis of the solid-gas type of reaction showed that only 83 percent

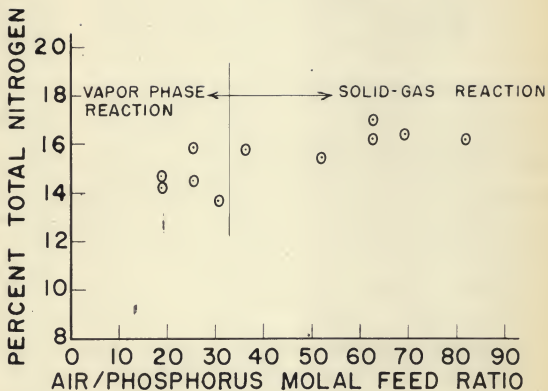


Figure 5. The effect of air to phosphorus molal feed ratios on the total nitrogen content of the product for a constant ammonia to phosphorus ratio of 2.

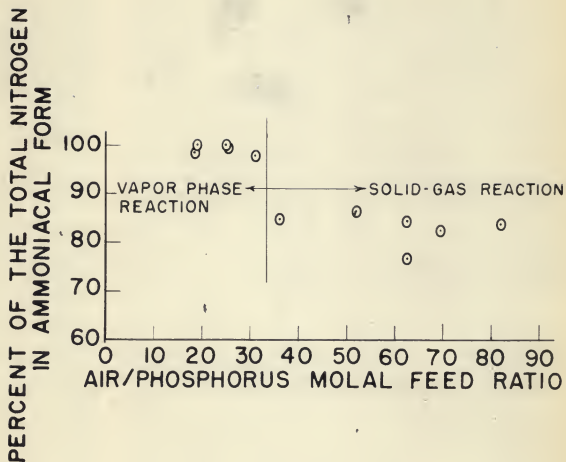


Figure 6. The effect of the air to phosphorus molal feed ratio on the fraction of the nitrogen existing in ammoniacal form for a constant ammonia to phosphorus molal feed ratio of 2.

of the nitrogen was in ammoniacal form. This indicates that the products from the solid-gas reaction contained either amido and imido groups as proposed by Van Wazer (17), or phosphoronitridic groups as proposed by Driskell (6). It may also be concluded that the NH_3/P ratio should not exceed 2.0. Operation with an NH_3/P ratio greater than 2.0 did not change the chemical content of the product. In equipment where the phosphorus feeding system was improved, the desirable NH_3/P ratio would be significantly different than 2.0.

Further studies into the effects of cooling the reactor would be of interest. As previously mentioned, when cooling was employed no product was recovered.

As previously mentioned, the electrostatic precipitator was used during the investigation of the effect of the flow ratio on the chemical composition of the products. The best operating conditions from these studies were used in the studies of other collection systems. This does not mean that the flow ratios were rigidly fixed but that the range of operation was determined.

The electrostatic precipitator proved to be an efficient means of collection. However, the high concentration of product and the resulting thick smoke resulted in rapid accumulation of the product on the walls and electrode of the precipitator. The overall result was that the precipitator required the attention of two people. Run lengths never exceeded 20 minutes. There were two reasons for the short period of operation. One is that sufficient product was collected in 20 minutes to supply material for analysis. The second is that product accumulation on the interior of the precipitator forced a shut down because of arcing. The product collected in the precipitator was light, fluffy and of very

fine particle size.

The bag filter proved as efficient as the electrostatic precipitator. The only maintenance required was to clean the bag at the end of each run. The product scraped from the bag was more dense than that obtained from the precipitator. Run lengths varied between one and two hours when the filter was used. The original data for the bag filter may be found in Table 3 in the appendix.

The bag filter was considered 100 percent efficient (collecting all of the product which entered the filter) and was used in combination with the various types of fluidized beds. The beds were evaluated to determine what percentage of the product entering was retained by the bed assuming that any material passing through the bed was stopped by the filter. Table 4 in the appendix is a summary of the data taken on the three types of fluidized beds studied. The auxiliary air was used in all runs employing fluidized beds to obtain the desired degree of fluidization or motion.

Run 1 was the fluidized bed alone. Operations of this type were always accompanied by some channeling at the bottom of the bed and violent slugging in the upper two-thirds of the bed. Many of the runs made on the fluidized bed alone had large slugs of solids transported up the column and into the filter. Some of these solids were retained by the filter and the rest dumped back into the column. Runs where this occurred could not be evaluated for collection efficiency and were not included in Table 4.

Run 2 was also the fluidized bed. The increased collection efficiency was due in a large part to the fact that the author tapped the column support with a rubber mallet during the entire run. The

purpose of this tapping was to simulate mechanical vibration. The tapping improved the behavior of the bed in that no slugs of material were transported into the bag filter. The violent slugging was not eliminated however.

In an attempt to reduce the violent slugging, a packed calming section was placed in the column beneath the bed. Preliminary tests using air as a fluidizing medium indicated that a very good quality of fluidization was obtained when the packed calming section was used. In run 3 the calming section was made up of 167 grams of one-inch berl saddles, followed by 1907 grams of ceramic balls $\frac{1}{8}$ -inch in diameter. A 1060 gram bed of product previously prepared was placed on top of the calming section. In actual operation, the combination of packed calming section and fluidized bed showed the highest collection efficiency. However, most of the material collected on the packing. The product collected on the packing until plugs were formed near the bottom of the packing. Plugging was followed by pressure increases in the reactor until enough back pressure was formed to clear the plugs. On occasion, the back pressure was sufficient to lift the bed and packing up into the filter. The plugging also caused intermittent flow through the system. The intermittent flow caused entrainment of burning phosphorus which at times was carried into the column. The entrained phosphorus caused contamination of the product.

Runs 4 through 7 were made with expanded metal baffles in the bed. In run 4 there were four baffles spaced at two-inch intervals amounting to a total baffled bed height of eight inches. The remainder of the bed behaved in a manner similar to that described in run 1. The four baffles did improve the collection efficiency however. The number

of baffles was increased to 13 (spaced two inches apart) for the remaining runs. The additional baffles had an obvious effect as is shown by the results from run 5. Run 6 was of short duration because an attempt was made to operate at a higher phosphorus feed rate and with a more quiescent bed. In other words, the smoke entering the bed was more dense and the motion of the particles in the bed less violent. The auxiliary air flow was reduced to accomplish this. The almost immediate result of this type of operation was plugging in the lower portion of the bed. Past experience dictated that the proper procedure in such instances was to cease operations. The collection efficiency compared favorably with run 4 in spite of the short operation. In run 7 the low efficiency was due to more than just random behavior of the bed, probably an error in measurement.

Considering the collection systems studied, the electrostatic precipitator and fluidized bed with packed calming section were eliminated from consideration for further study because of the need for constant attention and servicing. The bag filter worked the best on the small-scale work done here, but in larger installations the use of bag filters might lead to an almost batch-type of operation and frequent servicing. The fluidized bed with baffles showed a great deal of promise. Collection efficiencies as high as 66 percent were obtained in a single bed. The operation of the baffled bed was virtually trouble-free when the flow conditions were adjusted properly. The baffled fluidized bed would also lend itself to continuous operation where material could be continuously added to and withdrawn from the bed. Several beds combined in series would also increase the collection efficiency.

Plate VI shows a comparison of the fluidized bed and a baffled fluidized bed. The same air flow rates were used in both instances. The improved operation is obvious. The baffles eliminated the slugging entirely. Bubbles were formed as the gases passed up through the column, but the baffles served to break these up before they reached sufficient size to cause slugging.

The baffled fluidized bed also provides areas for future study. The effect of the relative amounts of bed initially present on the collection efficiency is one such area. The effect of particle size is another. A third area of possible investigation would be the relationship between particle size and opening in the baffle. The opening of the baffles might lead to a means for controlling the quality of a fluidized bed.

The results of the differential phosphate analysis were not too rewarding. Since the tests were used qualitatively, a positive test was the appearance of a precipitate. Definite tests for hexametaphosphate and trimetaphosphate were obtained. Van Wazer (17) indicated that hexametaphosphate is a misnomer. The term hexametaphosphate has been used to describe some sodium phosphate glasses with an M_2O/P_2O_5 ratio between one and two where $M = 1$ equivalent of cation. The test for pyrophosphate was the precipitation of manganous pyrophosphate. Small amounts of a brown precipitate were formed and since manganous pyrophosphate is brown, the test for pyrophosphate was considered positive.

Fig. 7 shows the results of the test for hygroscopicity and possible chemical reaction. The increase in dry weight indicates that reaction between the products and water vapor did occur. The fact

EXPLANATION OF PLATE VI

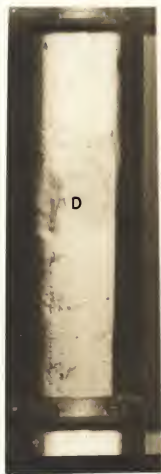
Illustrations Showing the Operation of the Fluidized Bed
with and without Baffles

- A. Fluidized bed with baffles
- B. Fluidized bed without baffles
- C. Bubbling
- D. Slugging
- E. Baffles

PLATE VI



A



B

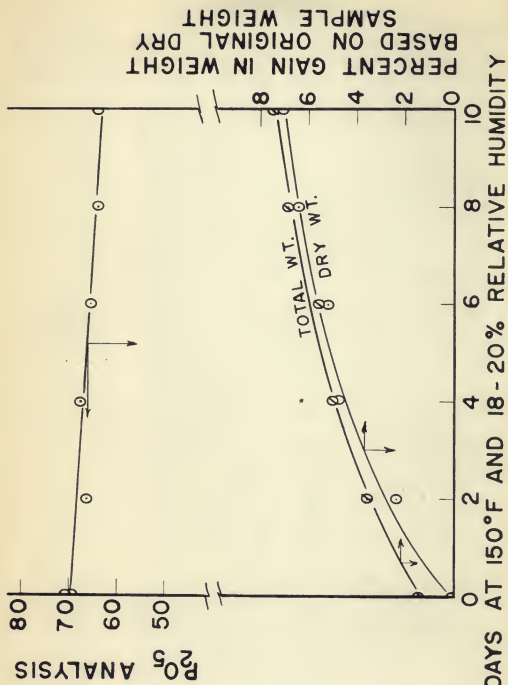
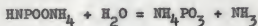
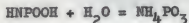
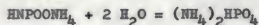
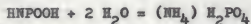


Figure 7. Results of the test for hygroscopicity and possible chemical reaction.

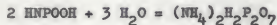
that the curves representing total weight gain and dry weight gain converge indicates that the moisture content was decreasing and the products were becoming less hygroscopic. The effect of the weight gain on the P_2O_5 content of the product was analyzed and the trend found to be significant. When the figures for P_2O_5 content were corrected for the weight gain, no significant trend existed. The results of this test correspond with the findings of Hignett, et. al. (9) and Stinson, et. al. (16). Hignett proposed the following equations to describe the reactions taking place between the products and water vapor:



If the compounds and their compositions in Table 1 are studied, it becomes obvious that the reactions proposed by Hignett could not have taken place in this instance. All of the reaction products proposed by Hignett have P_2O_5 analyses greater than 70 percent. Therefore formation of these products could not account for a decrease in P_2O_5 content to less than 70 percent as was the case here. For this reason, the following pairs of reactions are proposed to account for the reaction between the products of this study and water vapor. The starting compounds are phosphoronitridic acid and ammonium phosphoronitridate as suggested by Stinson, et. al. (16).



and



and



Table 1. Compositions of proposed reaction products.

Compound	Source (if any)	% P	% N	% P ₂ O ₅	Fraction of the Nitrogen present in ammoniacal form
NH_4PO_3					
Ammonium Metaphosphate	-----	31.95	14.43	74.20	1.00
$(\text{NH}_4)_2\text{P}_2\text{O}_7$					
Monoammonium Pyrophosphate	-----	31.79	7.17	73.83	1.00
$(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$					
Diammonium Pyrophosphate	-----	29.24	13.20	67.91	1.00
$(\text{NH}_4)_2\text{H}_2\text{PO}_4$					
Monoammonium orthophosphate	-----	26.95	12.17	62.59	1.00
$(\text{NH}_4)_2\text{HPO}_4$					
Diammonium Orthophosphate	-----	23.48	21.21	54.53	1.00
$\text{P}_2\text{O}_5\text{NH}_2(\text{ONH}_4)_2\text{OH}$					
Diammonium Amidopyrophosphate	Sanfourche	29.38	19.90	68.24	0.50
HNPOOH					
Phosphorotric acid	Driskell	39.24	17.72	91.13	0.00
HNPOONH ₄					
Ammonium Phosphorotric acid	Driskell	32.29	29.16	74.99	0.50
O					
$\text{NH}_2\text{-P-O-NH}_4$					
O					
$\text{NH}_2\text{-P-O-NH}_4$	Woodstock	26.95	24.34	62.59	1.00
O					

Table I. (Concl.)

Compound	Source (if any)	% P	% N	% P ₂ O ₅	Fraction of the Nitrogen present in ammoniacal form
$ \begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}-\text{NH}_4 \\ \diagup \quad \diagdown \\ \text{HN} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{P}-\text{O}-\text{NH}_4 \\ \parallel \\ \text{O} \end{array} $	Woodstock	32.12	21.76	74.60	0.67
$ \begin{array}{c} \text{O} \quad \text{H} \quad \text{O} \\ \parallel \quad \parallel \quad \parallel \\ \text{NH}_4-\text{O}-\text{P}-\text{N}-\text{P}-\text{O}-\text{NH}_4 \\ \mid \quad \mid \quad \mid \\ \text{O} \quad \text{O} \quad \text{O} \end{array} $	Woodstock	32.12	21.76	74.60	0.67
$ \begin{array}{c} \text{NH}_4-\text{O}-\text{P}-\text{N}-\text{P}-\text{O}-\text{NH}_4 \\ \parallel \quad \parallel \quad \parallel \\ \text{O} \quad \text{H} \quad \text{O} \end{array} $	Van Wazer	32.12	21.76	74.60	0.55
$ \begin{array}{c} \text{O} \quad \text{O} \quad \text{H} \quad \text{O} \quad \text{NH} \quad \text{O} \\ \parallel \quad \parallel \quad \parallel \quad \parallel \quad \parallel \quad \parallel \\ \text{H}_2\text{N}-\text{P}-\text{O}-\text{P}-\text{O}-\text{P}-\text{N}-\text{P}-\text{O}-\text{P}-\text{O}-\text{NH}_4 \\ \mid \quad \mid \quad \mid \quad \mid \quad \mid \quad \mid \\ \text{O} \quad \text{NH}_2 \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{OH} \\ \parallel \quad \parallel \quad \parallel \quad \parallel \quad \parallel \\ \text{NH}_4 \quad \text{NH}_4 \quad \text{NH}_4 \quad \text{NH}_4 \end{array} $					

One method of testing the two proposed sets of reactions would be to repeat the experiment and analyze the products for total nitrogen. If the tests showed a loss in nitrogen content, then the reactions proposed which formed pyrophosphates might have taken place. If there was no nitrogen loss the reactions forming orthophosphates might have occurred.

When the hygroscopicity tests were repeated using a water saturated atmosphere, the samples became liquid after one day. A sample exposed to the saturated atmosphere for one hour gained 13 percent in total weight but showed no significant decrease in dry P_2O_5 content. These results show that the product is quite hygroscopic, and that the reactions with absorbed water are relatively slow.

CONCLUSIONS

It is probable that two types of reactions occur. The first type is a vapor-phase reaction, which occurs at high temperature, and produces a product containing only ammoniacal nitrogen. The second type of reaction probably is a solid-gas reaction producing both ammoniacal and non-ammoniacal nitrogen in the products.

The air/phosphorus ratio determines the temperature in the reactor and therefore the type of reaction occurring. The relative amounts of air present did not affect the chemical composition of either type of reaction product, although the products of the two different reactions did differ in chemical composition.

The composition of the products was not changed with ammonia to phosphorus molal feed ratios above 2.0. Below this ratio, the amount of nitrogen in the products decreased.

The reaction products were hygroscopic in nature and of low bulk density. They also reacted with water vapor present in the atmosphere. This reaction and hygroscopicity would lead to storage problems. The reaction with water vapor produces materials which are less hygroscopic and more dense than the original. This is an area which deserves more work.

The fluidized bed with baffles demonstrated reasonably effective collection and showed promise for larger scale operations.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. William H. Honstead for his advice and guidance throughout this investigation. The author is also grateful for the advice given by Dr. Clifton E. Meloon on the colorimetric analysis, Dr. Arlin M. Feyerherm for aid in the statistics, and for the sponsorship of the Kansas State Agricultural Experiment Station.

LITERATURE CITED

1. Association of Official Agricultural Chemists.
Methods of Analysis, 7th ed.
Washington D. C., The assoc., 1950.
2. Bridger, G. L.; D. R. Boylan; and J. W. Markey.
Colorimetric determination of phosphorus pentoxide in
fertilizers using a standard calibration plot. Analytical
Chemistry 25, 336-338, 1953.
3. Christian, Curtis G.
Nitrogen-Phosphorus composition.
U.S. Patent 2,839,375, 1958.
4. Christian, Curtis G.
Nitrogen-Phosphorus compositions.
U.S. Patent 2,884,318, 1959.
5. Driskell, John C.; et. al.
Concentrated fertilizer material from phosphorus, air, and
ammonia.
Agricultural and Food Chemistry 7 No. 9, 618-622, 1959.
6. Driskell, John C.
Production of nitrogen-phosphorus compounds. U.S. Patent
2,713,536, 1955.
7. Eisenhart, C.
The interpretation of certain regression methods and their
use in biological and industrial research. The Annals of
Mathematical Statistics 10 No. 2, 62-186, 1939.
8. Getsinger, J. G.; E. C. Houston; and F. P. Achorn.
Production of diammonium phosphate by continuous vacuum
crystallization. Agricultural and Food Chemistry 5 No. 6,
433-436, 1957.
9. Hignett, Travis P.; et. al.
Nitrogen-phosphorus compounds.
U.S. Patent 2,856,279, 1958.
10. Jones, L. T.
Differential analysis of phosphate mixtures. Ind. Eng. Chem.,
Anal. Ed. 14, 536-541, 1942.
11. Jones, Otha C.; and P. G. Arvan.
Ammonia - phosphorus pentoxide reaction products.
U.S. Patent 2,717,198, 1955.

12. Monsanto Chemical Company.
Ammonia-phosphorus pentoxide reaction products. British Patent 729,243, 1955.
13. Rice, Owen.
Method for producing ammonium phosphate. U.S. Patent 2,561,415, 1951.
14. Ross, William H.; A. R. Merz; and J. N. Carothers.
Process for preparing a concentrated fertilizer. U.S. Patent 1,194,077, 1916.
15. Snedecor, George W.
Statistical methods, 5th ed. Ames, Iowa, Iowa State College Press, 1956.
16. Stinson, J. M.; et. al.
Ammonium metaphosphate fertilizer: pilot plant production and greenhouse tests of fertilizer from ammonia and phosphorus pentoxide vapors. Agricultural and Food Chemistry 4 No. 3, 248-253, 1956.
17. Van Wazer, John R.
Phosphorus and its compounds. Vol. 1, Chemistry. New York, Interscience Publishers, 1958.
18. Wang, Jih-Ming.
Studies on the gas phase reaction for the production of ammonium phosphate. Unpublished M.S. thesis, Kansas State University, 1959.
19. Winsor, Charles P.
Which regression? Biometrics Bulletin 2 No. 6, 101-109, 1946.
20. Woodstock, Willard H.
Water softener. U.S. Patent 2,122,122, 1938.

APPENDIX

Table 1. Summary of original data from electrostatic precipitator for constant phosphorus flow rate of 0.32 g-atoms/min.

Run No.	Ammonia : g-moles/min	Air : g-moles/min	Temperatures, : °F		Nitrogen: : Total	Analysis, : Ammoniacal	Phosphorus : Recovery
			T ₁	T ₂			
1	0.65	20.0	626	516	17.00	13.01	50.1%
2	0.65	12.5	698	578	a	a	d
3	0.65	12.5	596	483	a	a	29.2%
4	0.65	17.8	683	572	16.20	13.07	57.4%
5	0.65	22.1	608	520	16.42	13.54	51.4%
6	0.65	26.2	576	516	16.19	13.62	38.4%
7	0.65	16.6	559	535	15.38	13.34	45.9%
8	0.65	11.6	636	563	15.77	13.44	56.8%
9A	0.65	9.97	528	466	a	a	33.2%
9B	0.65	9.90	698	706	13.73	13.42	57.9%
10	0.65	8.07	777	734	14.53	14.38	58.5%
11A _b	0.65	6.03	828	829	14.27	14.25	35.7%
11E _b	0.65	5.95	896	858	a	a	--
11C _b	0.65	5.97	876	893	a	a	--
11D	0.65	5.99	924	813	14.67	14.53	61.9%
12	0.65	4.41	966	955	a	a	d
13	0.96	7.95	812	889	14.21	14.26	58.0%
14	1.07	8.04	817	849	15.53	15.49	49.9%
15	0.875	8.04	833	856	15.10	15.08	60.0%
16	0.46	8.13	786	769	14.31	13.85	60.4%
17	0.32	8.04	826	766	12.48	11.27	44.2%
18 ^c	0.65	8.00	817	693	15.91	15.87	25.2%

- a) Products not analyzed, results not used in body of report.
 b) Cooling attempted, no product collected.
 c) Water added to system at 0.32 gm-moles/min.
 d) Not determined.

Table 2. Summary of original data from temperature studies for a constant P flow of 0.32 g-atoms/min. and a constant NH_3/P molal feed ratio of 2.

Run No.	Air feed rate g-moles/min	Temperatures, $^{\circ}\text{F}$. ^a		
		T_1	T_2	T_3
1	7.99	770	673	525
2	8.04	755	662	525
3	9.20	718	635	516
4	9.24	710	620	510
5	12.62	600	577	477
6	9.89	697	640	515
7	8.11	745	665	527
8	11.57	615	605	596
9	9.35	675	632	507
10	10.52	633	620	502
11	11.32	600	595	487
12	12.59	660	621	518
13	9.83	753	667	558
14	9.27	692	608	509
15	8.68	724	629	510
16	8.06	760	650	525
17	11.57	588	542	461
18	12.42	656	620	572
19	11.42	735	678	573
20	9.77	726	631	517

a All temperatures taken from temperature recorder.

Table 3. Summary of original data from bag filter.

Run No.:	Phosphorus g-atom/min:	Ammonia g-moles/min:	Air g-moles/min:	Temperature, °F: T ₁	°F: T ₂	°F: T ₃	Phosphorus Recovery, %
1	0.185	0.382	9.93	700	635	510	68.0
2	0.184	0.382	10.01	725	630	520	83.5
3	0.20	0.382	10.29	775	700	570	64.9

Table 4. Summary of data from fluidized collectors.

Run No.	Description of collection system	Air/p molal feed ratio	Initial bed wt.	Mesh size range of particles in bed	Length of run	Final bed wt.	Percent of total collected by bed	Phosphorus recovery
1	Fluidized bed + bag filter	41.1	1592 g	-10 + 18	51 min.	1797 g	36.2	47%
2	Fluidized bed + bag filter	40.6	1543 g	-10 + 18	60 min.	1947 g	59.2	56%
3	Fluidized bed with packed calming section + bag filter	43.1	3134 g (packing + bed)	-18 + 30	40 min.	3277 g (packing + bed)	70.1	56%
4	Fluidized bed with baffles + bag filter	34.5	882 g	- 4 + 20	92 min.	1219 g	47.4	45%
5	Fluidized bed with baffles + bag filter	42.6	1597 g	- 4 + 20	66 min.	1990 g	66.3	57%
6	Fluidized bed with baffles + bag filter	33.3	1508 g	- 4 + 20	12 min.	1624 g	47.9	43%
7	Fluidized bed with baffles + bag filter	35.1	1185 g	- 4 + 20	60 min.	1325 g	29.5	52%

NITROGEN-PHOSPHORUS COMPOUNDS PRODUCED FROM THE
VAPOR-PHASE REACTION OF AMMONIA AND PHOSPHORUS PENTOXIDE

by

ALLAN H. MACDONALD

B. S., Northeastern University, 1959

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1961

The purpose of this study was to investigate the vapor-phase reaction between phosphorus pentoxide, ammonia, and water. The products of this reaction are nitrogen-phosphorus compounds which may be useful as fertilizer materials or as water softeners. Investigations into the effects of the relative flow rates of the reactants on product composition and studies of various collection systems were carried out with small-scale pilot plant equipment.

A great deal of variation was present in the experimental results due to the fact that the white phosphorus burned to form the P_2O_5 was partially converted to the more stable red form before reaching the combustion zone. The results of the study on flow rates did indicate the possibility of two different types of reactions occurring. The first, a vapor-phase reaction occurred when the temperatures in the system were above the sublimation temperature of P_2O_5 . The second type of reaction was between solid, finely divided P_2O_5 and gaseous ammonia occurring when the temperatures of the system were below the sublimation temperature of P_2O_5 . The temperatures were controlled by the relative amounts of air present. Ammonia to phosphorus molal feed ratios greater than 2.0 did not contribute to the composition of the products.

The reaction products as collected were dry and of low bulk density. Studies indicated that the products were hygroscopic and reacted with water vapor present in the atmosphere. The products of this reaction with water vapor are less hygroscopic and more dense than the products as originally collected.

The collection systems studied were an electrostatic precipitator, a bag filter; and a fluidized bed, a fluidized bed with a packed calming section, and a baffled fluidized bed. The three types of

fluidized beds were used in combination with the bag filter. Operating difficulties encountered with the electrostatic precipitator, the fluidized bed alone, and the fluidized bed with packed calming section would eliminate these collection systems from further consideration for larger scale operations. The bag filter proved to be the most efficient collector in these small-scale studies, but the baffled fluidized bed would appear to lend itself to large-scale continuous operations more readily than the bag filter.