

STUDIES ON THE GAS PHASE REACTION FOR THE PRODUCTION OF
AMMONIUM PHOSPHATE

by

JIH-MING WANG

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INTRODUCTION

The trend in the past decade in the chemical fertilizer industry has been to produce fertilizers and fertilizer materials of the highest possible plant nutrient content. Considerable research has been done and is still being carried out on different phosphorus, nitrogen and potassium carrying materials. Illustrative of this trend are the developments in concentrated superphosphate of 45 to 50% P_2O_5 , fused tricalcium phosphate of 26 to 30% P_2O_5 , diammonium phosphate with 54% P_2O_5 and 21% nitrogen and monoammonium phosphate with 11% nitrogen and 48% P_2O_5 . The high plant food value of the last two compounds together with their stability and their low hygroscopicity render them competitive with many other fertilizers since they carry a great advantage in their shipping, packaging and handling cost. These superior characteristics usually can offset their relatively higher cost of production over ordinary fertilizers (10) (12).

Various processes have been developed by the industry for the manufacture of mono and diammonium phosphate. These differ one from the other in their technical aspects (12), however, the general principle involved in the production is the same. Anhydrous ammonia is absorbed in phosphoric acid made either by the wet process or from elemental phosphorus. For high grade monoammonium phosphate, the process uses a continuous, single-stage saturator similar to that used in the manufacture of by-product ammonium sulfate. By starting with 75% phosphoric acid, a pasty mass results from which crystalline monoammonium phosphate can be obtained by cooling, centrifuging and drying (1)(11). Fertilizer-grade monoammonium phosphate may be made batchwise from wet-process phosphoric acid and

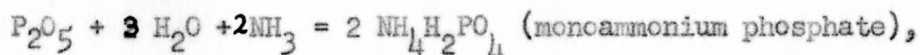
ammonia liquor from by-product coke manufacture. The liquor is fed into the circulating batch until a resultant slurry is formed that can be pumped through pipelines. The production of this kind of granular concentrated fertilizer has been developed by the Dorr Company (13)(14). A special feature of this process is the use of some sulfuric acid in addition to phosphoric acid. By varying the relative quantities of these two acids, the N_2 to P_2O_5 ratio of the finished product can be varied from a straight monoammonium phosphate containing about 11 to 12% nitrogen and 48 to 52% P_2O_5 to pure ammonium sulfate with 21% nitrogen. The intermediate products consist of mixtures of ammonium phosphate and ammonium sulfate of such compositions as: 18-18-0, 16-24-0, 15-30-0 and 13-39-0.

In most processes for the manufacture of diammonium phosphate, phosphoric acid is neutralized with ammonia in two stages instead of only one stage as in the production of monoammonium phosphate. When wet-process phosphoric acid is employed, the first stage of the introduction of ammonia results in the precipitation of the bulk of the iron, aluminum, fluorine, calcium and magnesium which are present. These impurities can then be removed by filtration. The filtrate which consists of a practically pure solution of monoammonium phosphate is evaporated and then saturated with ammonia to an NH_3 to P_2O_5 mole ratio of 2:1. The product is then crystallized, centrifuged and dried. The equipment required in this process is similar to that described for the manufacture of the mono-basic salt.

Thus in order to produce either diammonium or monoammonium phosphate, there invariably are involved many steps of unit operations such as gas absorption, mixing, evaporation, crystallization and drying etc. It is always one of the objects of chemical engineers to modify the manufacturing

processes in order to get the same end products with less fixed investment and lower production costs. This work was undertaken for this reason.

In the following simple reaction equation,



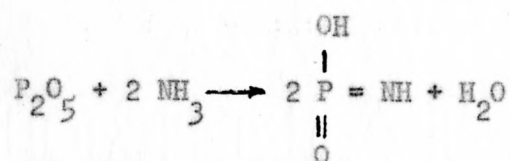
phosphorus pentoxide vapor, obtained from the oxidation of elemental phosphorus in an air stream, reacts with water and anhydrous ammonia (mole ratio $\text{P}_2\text{O}_5:\text{H}_2\text{O}:\text{NH}_3 = 1:3:2$) to give two moles of monocammonium phosphate. If the water is present as vapor, the reaction will occur in the vapor phase and since the product is a solid, the reaction equilibrium should be favorable. Even though the above reaction may not represent the true course of events, some combination of nitrogen and phosphorus suitable for use as plant food may be found.

If such a scheme for producing N-P fertilizers were successful, it would have the great advantage of simplicity of operation. In other words, it would avoid the use of many large and expensive pieces of equipment such as agitators, crystallizers, centrifuges and dryers. It is also obvious that such operation would cause a substantial saving in the production costs as well as in the initial investment. It is with this motive that the present investigation was initiated. As this is a typical bench-scale research problem, its chief emphasis was on the effects of various reaction conditions on the products formed.

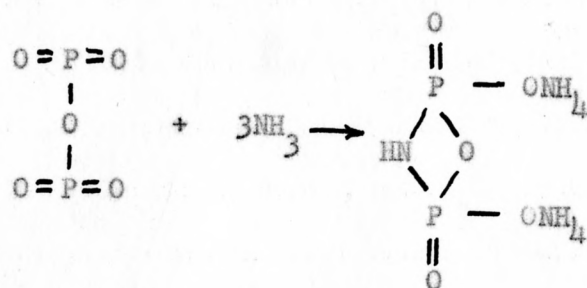
LITERATURE SURVEY

The reaction behavior of phosphorus pentoxide toward anhydrous ammonia has been repeatedly studied by various researchers in many countries over

a long period of time. Unfortunately even up to the present time, it is still impossible to obtain a definite reaction product. According to Fischer (5), Schiff in Germany, who published a paper in 1857, was the pioneer in this field. He named the reaction product phosphaminic acid (actually a simple imidophosphoric acid) with appearance very similar to red phosphorus. He formulated the reaction as:

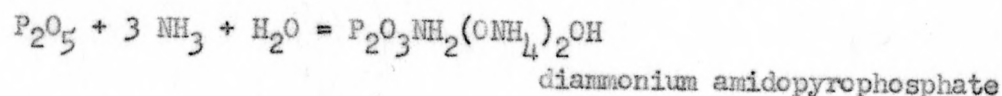


but through the works of Gladstone and Mente, the existence of this compound became very doubtful. Mente said the reaction occurred according to:

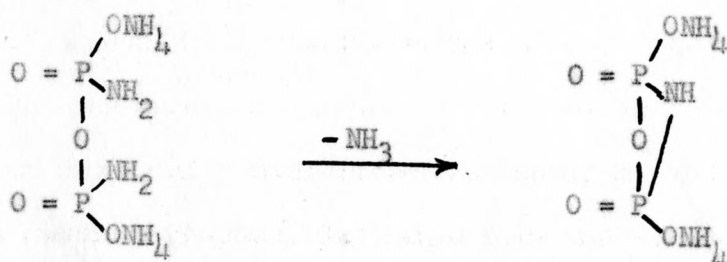


There was also formed ammonium pyro- and ammonium metaphosphate.

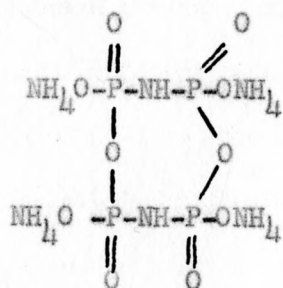
Later in 1930, Sanfourche, et al., is reported by Fischer (5) to have burned red phosphorus with a mixture of air and nitrogen. Ammonia was added to the combustion products and the reaction product was collected in jars. They investigated the effect of the amount of moisture in the combustion air and found that they obtained low yields of products when they used artificially dried air. They postulated their reaction as



Woodstock (15) in 1938 described the reaction of ammonia gas, preferably at elevated temperatures, with solid phosphorus pentoxide suspended in paraffin oil for the purpose of developing a kind of water softening agent. He postulated that the active component of the reaction product was a diammonium salt of diamidopyrophosphoric acid, which upon further heating was assumed either to eliminate ammonia and change into a 4-member ring



or else two molecules of ammonia were lost and the product condensed to



All the statements of Woodstock on the structure of his products were no more than guesses, since the proof for his postulates was only the molar ratio of total nitrogen to phosphorus in the product.

Still later, Fischer (5), in view of the fact that certain products of P_2O_5 and ammonia, or loose ammonia compounds, all possess the ability to form complexes with calcium and magnesium to act as water softeners, did an extensive study of the method of producing different preparations to clarify their constitution and further to investigate their behavior

toward the hardness formers in water. He started his work by purifying phosphorus pentoxide. Usually commercial phosphorus pentoxide is a mixture of various modifications, the individual existence ranges of which are still very unclear. The various kinds of P_2O_5 differ from each other very considerably in their volatility as well as in their reaction behavior, therefore, it is necessary to get it as pure as possible. He employed both sublimation and extraction, however neither was successful since he could not obtain an absolutely suboxide-free phosphorus pentoxide. He investigated the reaction between phosphorus and ammonia under various conditions and also with various forms of these two reactants. Among the solid NH_3 -donors used were urea, sodium amide and ammonium carbamate. Among the reaction systems used were P_2O_5 with liquid ammonia; the oxidation of phosphorus vapor in the presence of gaseous ammonia, and the reaction of P_2O_5 suspended in a liquid such as carbon tetrachloride or paraffin oil with ammonia at elevated temperatures. He found that, with the latter system, the reaction started at the boundary surface between the phases of the two reactants, from where it penetrated into the interior of the pentoxide particle. That is, an impervious coating was formed on the surface of the particle which prevented further reaction with ammonia. Under these circumstances, it was impossible to obtain a homogeneous product with a definite chemical structure. The conclusion was reached that if the reaction could be conducted in the vapor phase, a better reaction product might reasonably be expected.

He therefore changed his approach to this direction. He found that at elevated temperatures, when the phosphorus pentoxide vapor carried by

an oxygen stream was condensed in an ammonia atmosphere, a flour-fine white powder precipitated.

From his preliminary experiments, Fischer knew that the ammonia must have mixed with the pentoxide vapor since the X-ray diffraction pattern of the reaction product no longer exhibited any pentoxide line. This could only be attained if the two substances came together at the same temperature, because if the pentoxide condensed prematurely in contact with cold ammonia, the transformation between ammonia and solid pentoxide would remain incomplete. For this reason he also heated the ammonia gas before introducing it into the over-heated part of the sublimation tube in which solid P_2O_5 was sublimed.

In addition to the product of extremely fine-grained powder, a yellow glass was also reported to be present in fairly large quantities. Though the purity of the sublimation product was superior to all of the other methods of preparations, the yield obtained was extremely small. The losses were due to the unsublimable residue which constituted at least two-thirds of the pentoxide sample and also to the premature reaction between solid P_2O_5 and NH_3 which hindered further sublimation.

Fischer used the conventional procedures of analysis including the determination of P_2O_5 , ammonium nitrogen and total nitrogen. These could not allow him to draw reliable conclusions on the structure of the products. Therefore he attempted to convert the reaction products into crystallizable alkali salts or into metal salt precipitates as the best means to prove their structural constitution. He first tried to recrystallize the products occurring in the form of the ammonium salt from water

or from excess ammonium alkali solution. However, they exhibited such a high solubility or tendency to supersaturation that a crystallization could be attained only after a very long period of time. At very high concentrations, however, a simple ammonium salt, free of directly bound nitrogen, was reported to be crystallized out.

The precipitations with 2- or 3- valent metal ions such as calcium and magnesium, however, gave barely soluble precipitates of a voluminous jelly-like nature. It was desirable to exclude the possible simultaneous precipitation of the corresponding metaphosphates due to the unreacted pentoxide residues. However he was unable to find conditions under which he would get nitrogen phosphoric acid without also getting metaphosphoric acids. He claimed that even when a pure separation of metaphosphate was dispensed with, the isolated form of the precipitates were still so unfavorable, due to their extremely difficult washing-out process that it was impossible to reach a conclusion on their constitution through the use of metal salts.

Further, the precise bond form of the directly bound nitrogen, whether in NH_2^- , NH^- , $\text{NH}^=$, NH_2^- , NH^- , $\text{NH}^=$ or even NH^{\equiv} groups, also remained uncertain. This is of course, no criterion for distinguishing between amido and imido groups in inorganic compounds as in organic compounds.

Fischer performed his investigations under thoroughly moisture-free conditions. He dried the ammonia carrier gas, such as oxygen and nitrogen, as completely as possible. Remaining traces of water vapor might have reacted catalytically but could not have participated decisively in the transformation. This is somewhat contrary to Sanfourche and co-workers' reasoning that water vapor is a decisive participant in the reactions.

Fischer was successful in confirming experimentally what Woodstock had surmised, that the reaction products were polymers. He applied the freezing point depression method to compare with that of pure acidic pyrophosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$. The measured depression served as a criterion of the size of the phosphate polymers. The results indicated that high temperature products approach hexametaphosphate with respect to polymerization. It is also interesting to note that the calcium-binding ability increases with increasing polymerization.

All in all, Fischer reached the following conclusions, which were not in contradiction with those of previous investigators:

- (1) At room temperature NH_3 and P_2O_5 principally form diammonium salts of nucleus-substituted pyrophosphoric acids in which the type of bond of direct-bound nitrogen still remains unclarified.
- (2) At higher temperatures the primary products polymerize to larger molecules and therewith increase their ability to bind calcium and other metal ions into water soluble complexes.

Owing to the many different reactions possible, it is to be expected that many different products with respect to composition and structure would be obtained. Besides the white fluffy powder usually formed, Rice (9) patented a process for the production of a crystalline material having a unique and reproducible X-ray diffraction pattern. He claimed that this compound had the chemical formula, NH_4PO_3 , (ammonium metaphosphate). The main features of his process were:

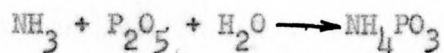
- (1) Elemental phosphorus in the molten condition was supplied to a combustion or reaction chamber to which atmospheric air containing water vapor for burning the phosphorus to pentoxide and ammonia gas

was supplied. These streams were adjusted adequately so that an ammonium phosphate product was collected on filter surfaces.

(2) The reaction had to be quickly cooled or otherwise the reaction products would decompose to a sticky, viscous, and highly hygroscopic substance. The reaction temperature was kept below 900° F as ammonia decomposes above this temperature.

(3) The ratio of ammonia to phosphorus was varied from 0.65:1 to 2:1 on a weight basis.

He also introduced into the air supply, liquid water as a mist in addition to that which was already present in the atmospheric air. Within the limit of the capacity of the apparatus, he found even a 900 per cent excess of water (10 times greater than the amount theoretically required to form NH_4PO_3 from the theoretical amounts of P_2O_5 and NH_3) did not impair the proper functioning of his system and did not appear to be critical with respect to the successful operation of the process. However, the process was critical with respect to lack of moisture, since enough water and ammonia were necessary for the reaction to proceed to ammonium metaphosphate phosphate according to the equation:



Rice later, in another patent (8), claimed to have made improvements and modifications of his first invention.

The processes in which phosphorus is burned with air containing water vapor have the disadvantage that a poor phosphorus recovery is obtained. The reason for such poor recovery is that water vapor in the combustion air reacts with phosphorus pentoxide to form metaphosphoric acid. This acid collects in the form of highly viscous, glassy material. The

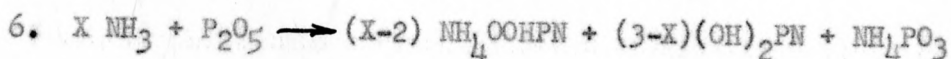
formation of this acid constitutes not only a loss of phosphorus to the process, but it gives rise to a difficult problem of removing it from the combustion chamber. Therefore, Driskell (4) invented a new process for reacting ammonia and phosphorus pentoxide without any appreciable amount of moisture present. Air was dried first to a moisture content of less than 0.00008 pounds water per pound of dry air. Then elemental phosphorus was oxidized with this dried air. The reaction products were cooled to a temperature of 550° to 700°F, then reacted with ammonia in the proportion of from 2.1 to 2.7 moles of NH_3 per mole of P_2O_5 . Driskell postulated that the reaction products were a mixture of ammonium metaphosphate, NH_4PO_3 , phosphoronitridic acid, $(\text{OH})_2\text{PN}$, and ammonium phosphoronitridate, $(\text{NH}_4\text{OOHPN})$. These compounds resulted from a combination of several chemical reactions:

1. $\text{P}_2\text{O}_5 + 2 \text{NH}_3 \longrightarrow 2(\text{OH})_2\text{PN} + \text{H}_2\text{O}$
(phosphoronitridic acid)
2. $(\text{OH})_2\text{PN} + \text{H}_2\text{O} \longrightarrow \text{NH}_4\text{PO}_3$
(ammonium phosphate)
3. $(\text{OH})_2\text{PN} + \text{NH}_3 \longrightarrow \text{NH}_4\text{OOHPN}$
(ammonium phosphoronitridate)

If any water in the system was free to react with phosphoronitridic acid and phosphoronitridate to form metaphosphate, the following reactions could occur:

4. $(\text{OH})_2\text{PN} + \text{H}_2\text{O} \longrightarrow \text{NH}_4\text{PO}_3$
5. $\text{NH}_4\text{OOHPN} + \text{H}_2\text{O} \longrightarrow \text{NH}_4\text{PO}_3 + \text{NH}_3$

The overall reaction between NH_3 and P_2O_5 , assuming that no water was added to the system, might be represented as:



where X is a number between 2 and 3.

If $X = 2.3$, the product theoretically would contain:

| | |
|---------------------------|-------|
| NH_4OOHPN | 15.9% |
| NH_4PO_3 | 53.6% |
| $(\text{OH})_2\text{PN}$ | 30.5% |

and the theoretical ratio of ammonical nitrogen to total nitrogen would be 0.565. However since it was impossible to avoid the addition of some water, the actual composition of the product differed from the theoretical in that it contained a larger proportion of ammonium metaphosphate and a smaller proportion of phosphoronitridic acid and ammonium phosphoronitridate.

Though Driskell made an elaborate postulation of the reaction mechanism based on the composition of his reaction products, there was no positive proof that the reactions go just the way he assumed.

Monsanto Chemical Company, one of the big companies in phosphate manufacturing, have also shown their interest in this specific reaction for the purpose of developing a nitrogen-phosphorus containing fertilizer and/or an efficient water softener. In their U. S. Patent 2, 717, 198. by O. C. Jones et al., (6) they thoroughly reviewed the previous literature. It seemed to them that no method of preparation other than the vapor phase reaction that Herbert Fischer investigated was free of a number of technical or commercial disadvantages. It was well known that many different products are obtained from the reaction of gaseous ammonia and phosphorus

pentoxide, depending upon the condition under which the reaction is carried out. If they are allowed to react under anhydrous conditions, reaction complexes are formed such as Driskell claimed. On the other hand, when the reaction is carried out in the presence of moisture, ammonium metaphosphate is obtained. Monsanto's patent is primarily concerned with the former type of product in which the NH_3 to P_2O_5 molar ratio is in excess of two to one, and water is not a reactant.

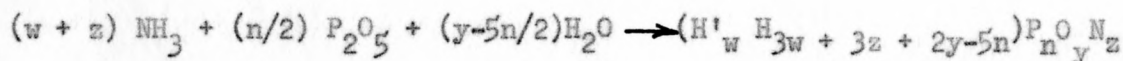
In the Monsanto patent, ammonia was reacted with phosphorus pentoxide produced by burning phosphorus in an excess of dry air. The reaction products were cooled rapidly. As the reaction temperature was increased from 240°C to 725°C , the products obtained within this range, decreased in water solubility. For convenience, they may be classified as a high temperature form and a low temperature form.

In the production of the low temperature form, the reaction was carried out at a temperature range from 325°C to 350°C and the NH_3 to P_2O_5 mole ratio varied from 2.2 to 1 to 3.2 to 1. This low temperature water soluble product was subjected to a calcination for 1 to 3 hours at 100°C while in contact with an atmosphere of ammonia. This resulted in the production of a product of substantially increased solubility in water. The purpose of the calcination was to obtain a product with a higher average molecular weight, to increase the ammonia content and to enhance its water solubility and calcium repression power.

In preparing the high temperature form, the temperature range was 675°C to 700°C , and the NH_3 to P_2O_5 ratio was the same as before. The same calcination treatment was used. The water solubility decreased with

an increase in calcination temperature, reaching a minimum solubility at 250°C to 300°C.

Van Wazer (16) described the reaction products as chain phosphates having some amido and imido groups. Study of these products showed that they were rather complicated mixtures of a number of different molecules. A general formula for the reaction products suggested by him is $(N'_w + H_x) P_n O_y N_z$ in which N' is the ammonium nitrogen (not directly bonded to the phosphorus) and N is nitrogen (H_2N- , $NH-$, and $-N$) attached to the phosphorus. An over-all equation for the reaction was also proposed by him:



where $y \geq 5n/2$ and $(y + z)/n \geq 4$.

He also stated that the characteristics of the reaction products and their compositions were controlled by adjusting the following reaction conditions: (1) the $NH_3/H_2O/P_2O_5$ ratios, (2) the temperature of the P_2O_5 vapor, (3) the time interval between mixing the NH_3 and H_2O with the P_2O_5 and quenching the products. Unless the $NH_3/H_2O/P_2O_5$ ratio corresponds quite closely to that of the ammonium orthophosphate, the products are usually amorphous or show only a few X-ray diffraction lines belonging to the ammonium phosphates. Throughout most of the region of composition corresponding to an NH_3/P_2O_5 mole ratio between 0 and 2, the product is an amorphous white material, a significant fraction of which may be insoluble or slowly soluble in water.

MATERIALS AND METHODS

Materials

The elemental phosphorus used conformed to National Formulary specifications and was purchased from the Fisher Scientific Company either in one-pound or eleven-pound double tin packages. It was in the form of light yellow, wax-like sticks, $5/8$ inch in diameter and was kept under water for safe storage and shipment.

Anhydrous ammonia was obtained from a conventional cylinder containing 100 pounds of ammonia. The cylinder was fitted with a suitable regulator to control the pressure in the feed line.

The chemicals used in the analytical work were all analytical reagent grade.

Equipment

A schematic diagram of the equipment used in this investigation is shown in Plate I. It consisted of the following items:

- (1) The tube reactor, which was made of two-inch stainless steel pipe seven feet in length. The combustion of phosphorus as well as the vapor phase reaction was carried out in this tube reactor. The reactor was held in a horizontal position by two angle iron legs. The reactor was closed at one end by a stainless steel pipe cap, through which the tube carrying the reaction air was introduced. The end of the tube was curved at a right angle to its longitudinal axis so that the air was injected into the tube tangentially. This caused a swirling motion in the air stream and

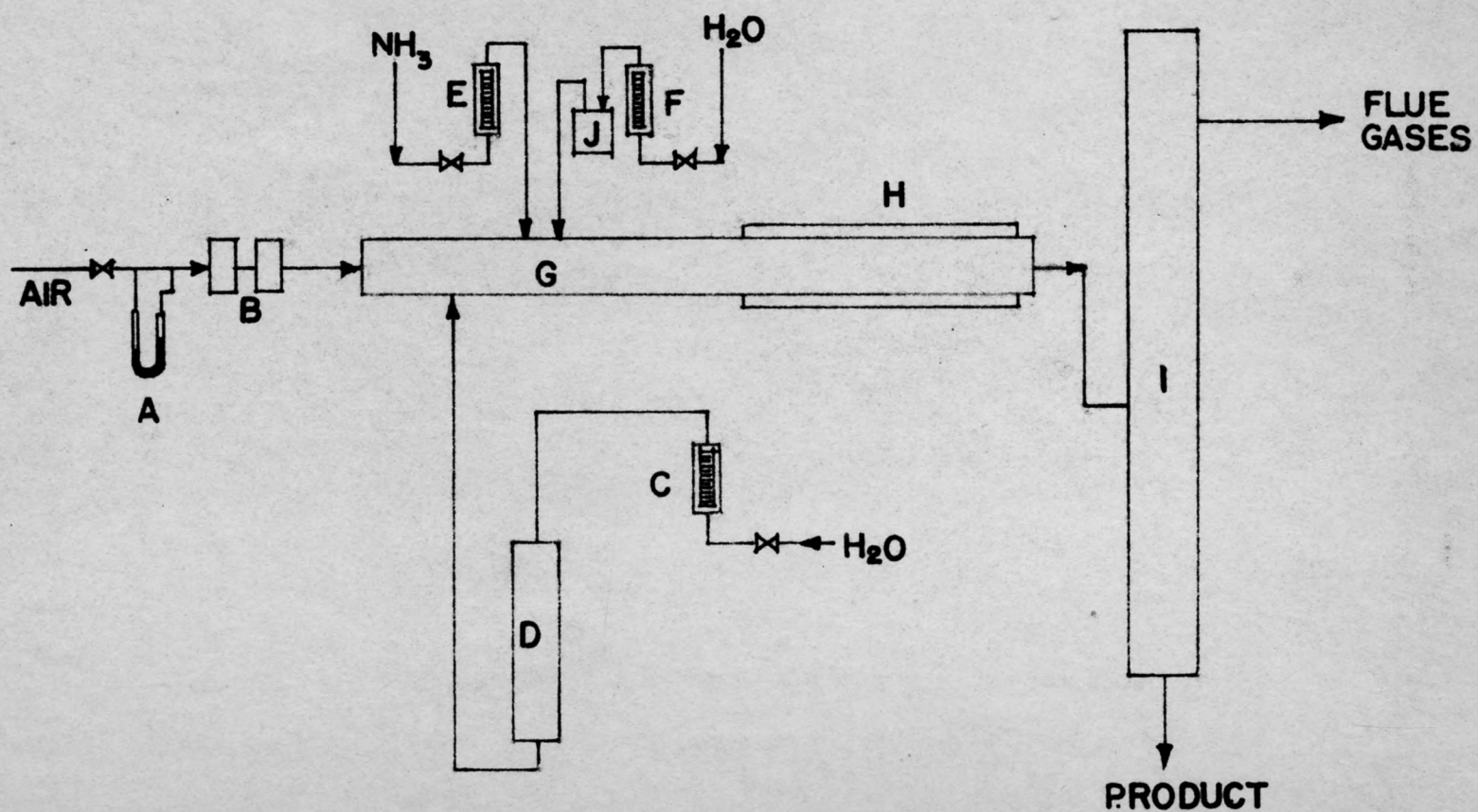
consequently a more efficient combustion; also a better mixing of the combustion products with the ammonia and steam were obtained.

EXPLANATION OF PLATE I

Schematic Diagram of Experimental Apparatus

- A. Air flow manometer
- B. Air drier
- C. Water displacement flowrater
- D. Phosphorus melter
- E. Ammonia flowrater
- F. Water flowrater
- G. Phosphorus combustion and reaction chamber
- H. Water cooler
- I. Collector
- J. Steam generator

PLATE I



The molten phosphorus inlet line as well as the ammonia and steam lines were located as shown in Plate II. The steam was metered as liquid water by a rotameter into a small boiler, where it was converted to vapor before entering the reactor.

Two thermocouple wells for temperature measurement of the combustion zone and reaction zone were provided on the tube reactor. Chromel-Alumel thermocouples were used with a Leeds & Northrup potentiometer for this purpose.

(2) The phosphorus melter, which was made of a section of two-inch stainless steel pipe, 14 inches long with caps on both ends. A 3/16-inch stainless steel tube was connected from the bottom of the melter to the reactor.

The molten phosphorus was forced into the reactor by water pressure above the melt. The phosphorus was metered by measuring the water entering the melter with a rotameter. The whole melter was immersed in a water bath inside of which an open steam coil supplied the necessary heat to keep the phosphorus molten.

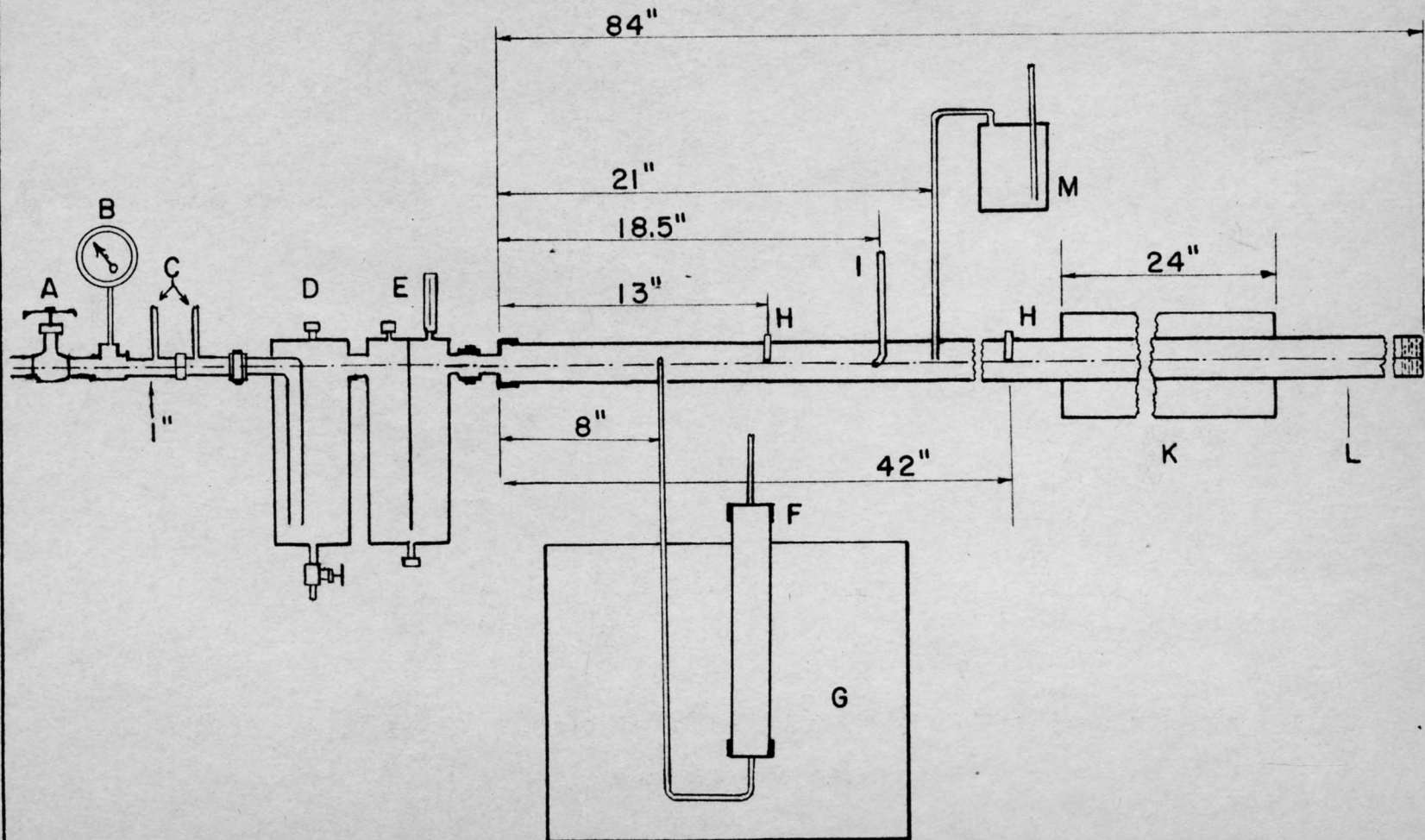
(3) The collector. A high voltage (40 KV) electrostatic Cottrell precipitator obtained from the Research-Cottrell Corporation, Bound Brook, N.J., was installed at the discharge end of the tube reactor. This unit provided an effective means for collection of the ultra-fine solid reaction products from the gas stream. A diagram of the precipitator unit and its operating principle is given in Plate III. It contained (A) a high voltage power pack, including a control cabinet, a set of high voltage transformers, a rectifier unit and the necessary controls and fuses; (B) an outer, grounded metal tube or shell as a collecting electrode; and (C) a metal rod mounted co-axially within the tube to which was applied

EXPLANATION OF PLATE II

Drawing of the Stainless Steel Pipe Reactor and Accessories

- A. 1" globe valve
- B. Air pressure guage
- C. Air flow manometer
- D. Air drier
- E. Acid mist separator
- F. Phosphorus melter
- G. Water bath
- H. Thermocouple wells
- I. Ammonia inlet
- K. Water cooler
- L. 2" ϕ stainless steel pipe reactor
- M. Steam generator

PLATE II

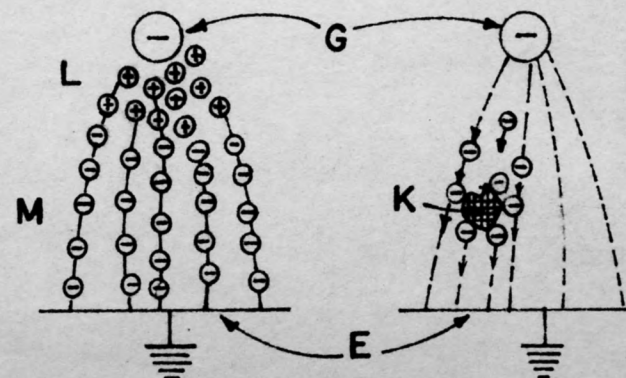
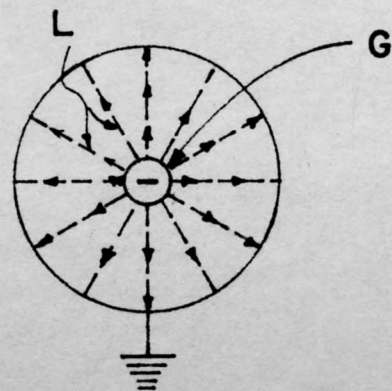
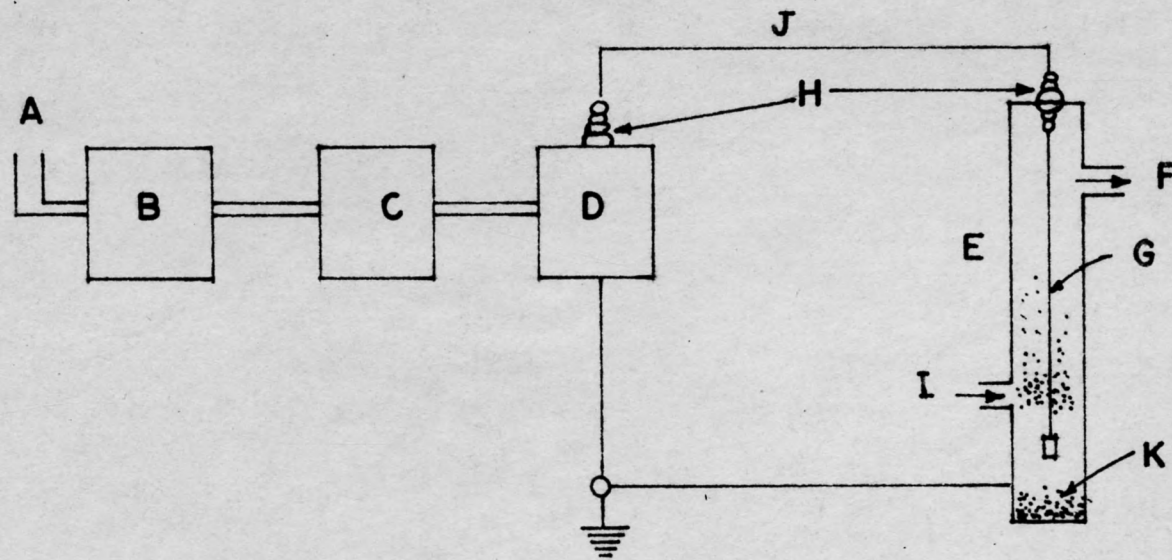


EXPLANATION OF PLATE III

Operating Principle and Diagram of an Electric Precipitator

- A. Power supply 220 V, 60 C single phase
- B. Control cabinet
- C. High voltage transformer
- D. Rectifier
- E. Collecting electrode shell (grounded)
- F. Flue gas outlet
- G. Emitting electrode wire
- H. Insulators
- I. Particle-laden gas inlet
- J. D.C. 40 KV (negative)
- K. Collected particles
- L. Paths of migrating ions

PLATE III



a high D-C voltage of negative polarity with relation to the grounded tube. The precipitator used in the present investigation was constructed of a 6-inch diameter inner tube, which served as the collecting electrode, and a 17-inch diameter outside shell as a steam jacket. This was not used in this work. It was supported by four legs adjusted so that the precipitator was held vertically. Its total length was 16 feet, 9 inches. A drawing of its construction is shown in Plate V.

The discharge electrode was of the prong and star type. It was made of 5/8-inch steel rod 9 feet, 7 inches long. It was fastened to a discharge electrode support which was suspended from the insulator conductor rod and was located in the exact center of the collecting pipe to maintain an even distribution of electric charges on the electrode. In order to prevent the shorting of the insulator due to moisture condensation in the gas stream, a steam coil was provided around the top of the discharge electrode fixture for maintaining the gas stream temperature in this region above the dew point.

A detailed diagram of the circuits in the power pack is shown in Plate IV. The high voltage connection was made at the top of the conductor rod protruding out of the top of the insulator by a length of 50 feet of high voltage cable. The other end of the cable was connected through a hole in the side of the power pack cabinet at the point marked "40 K.V. out" on the diagram.

EXPLANATION OF PLATE IV

Wiring Diagram of the Electrical System of the Precipitator

- S₁ Interlock switch rear door operated
- S₂ Main circuit breaker
- S₃ Capacitor shorting switch rear door operated
- S₄ High tension shorting switch rear door operated
- S₅ Milliammeter shorting switch
- R₁ 2-14 V, 420 watt parallel resistors
- R₂ 3-15 KV, 160 watt shunt resistors
- R₃ 150 V, 40 watt shunt resistor
- C₁ 0.1 M.F.D., 20 KV capacitor
- C₂ 1.0 M.F.D., 1 KV capacitor
- P₁ 2 KVA powerstat
- F₁ & F₂ High tension primary fuses
- F₃ & F₄ Filament primary fuses
- F₅ Milliammeter fuse
- T₁ High tension transformer, 200 V/15 KV

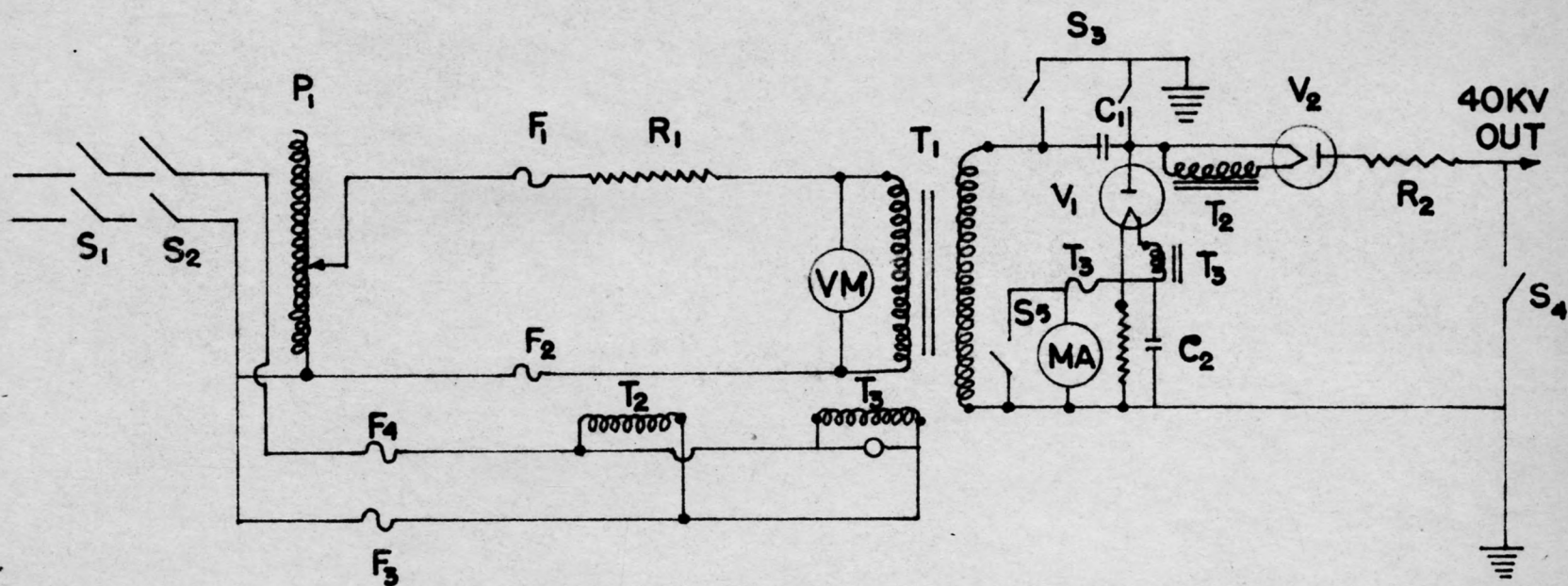
EXPLANATION OF PLATE IV

(Continued)

T_2 & T_3 Filament transformers, 200 V/5 V

V_1 & V_2 G. E. type 6L 8020 vacuum tubes

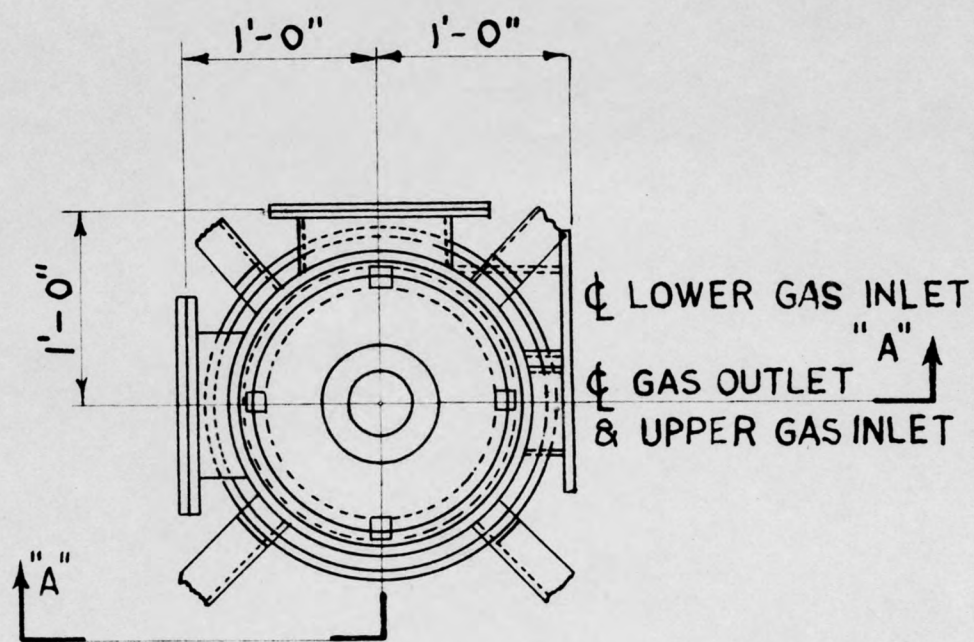
PLATE IV



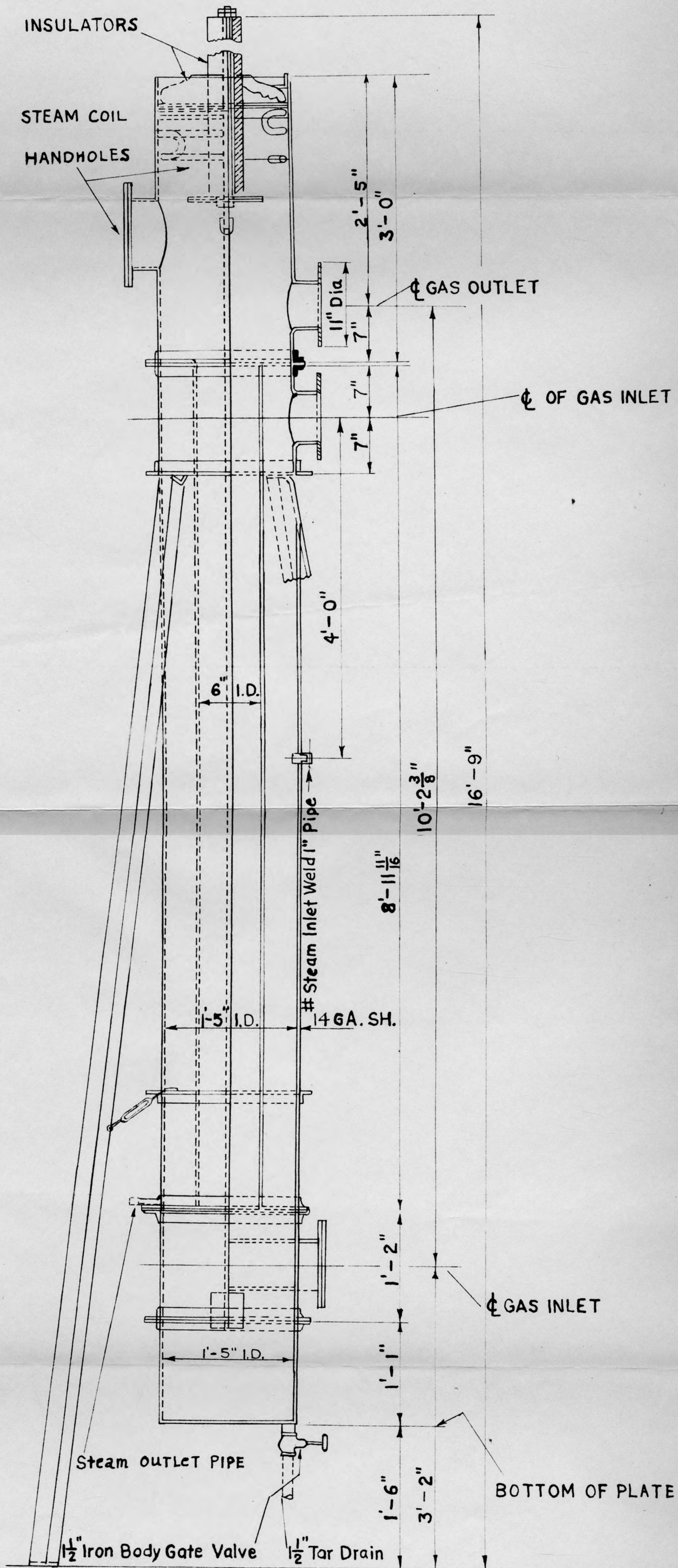
EXPLANATION OF PLATE V

Drawing of the Electric Precipitator

PLATE V



PLAN



SECTIONAL ELEVATION "A-A"

EXPERIMENTAL METHODS

Before the start of each run, about one pound of elemental phosphorus was charged into the melter. Since this chemical is poisonous to the human body as well as a very dangerous fire hazard, extreme care was exercised in its handling. In order to avoid physical contact with the phosphorus, because of its toxicity, tongs were always used for transferring the sticks into the melter. The time of exposure of the phosphorus to air during transfer was kept as short as possible. The cap of the melter was then screwed on tight so that no leakage occurred. This was important in order that a constant and accurate flow of molten phosphorus be ensured. The melter was then placed in the water bath at temperatures in the range of 50 to 55°C. White phosphorus melts at 44.1°C, therefore the bath temperature was high enough to assure its molten state. The phosphorus line was then heated by applying the flame of a gas burner, and the water for displacing the phosphorus was started. The air, ammonia, and the steam, if it was needed, were all turned on. When the phosphorus started to burn in the reactor, the temperature increased rapidly, finally reaching an equilibrium state. After running a few minutes, the power line switch of the power-pack unit was turned on, and the voltage on the electrode in the collector slowly increased until a slight discharge occurred in the collector as shown by a small current on the milliammeter on the control panel, and the disappearance of the white smoke from the exit gases. Usually an input voltage of 190 volts was used; this corresponded to about 32 KV on the electrode.

During the run, the reaction products were collected on the wall of the inner tube of the precipitator as well as on the metal electrode.

As more and more material was deposited, the gap between the electrodes and the walls became smaller and smaller. Eventually arcing occurred in the collector. When this happened, it was necessary to reduce the primary transformer voltage until the flash stopped. Usually about five minutes of collection was obtained before this happened. At the end of this period, the collector and the phosphorus, air, ammonia and steam lines were shut off.

At any time when work was to be done on the precipitator or in the power-pack compartment, the rear door of the power pack was opened. This automatically actuated a grounding switch which shorted out the high voltage circuits. Besides this safety device, two grounding chains with wooden handles were provided. One was kept within reach of the precipitator high voltage inlet, the other at the power pack.

After the shut down of the precipitator, the whole system was grounded, and the bottom plate removed. A length of cord with a bristle brush fastened to it was put into the inner shell through the handhole at the top. The white fluffy reaction products were brushed down by raising and lowering this brush. They were collected at the bottom of the precipitator and stored in quart jars.

Under some reaction conditions, a sticky liquid was formed on the inner shell. When this happened, the whole system (including the tube reactor and precipitator) was cleaned with water and air blown to dryness.

Methods of Analysis

Since the reaction products obtained were of primary interest as phosphorus fertilizers, the analytical methods used were not designed to

identify compounds or structures, but only to evaluate the plant nutrient value of the products. Methods for the analysis of fertilizers were therefore adopted in this investigation.

Moisture Determination. Approximately one gram of the sample was weighed into a regular weighing bottle that had been weighed to four decimal place accuracy. The bottle was dried in a constant temperature oven at 110° for exactly four hours. It was then placed in a desiccator to cool and finally reweighed. The loss in weight was reported as the per cent moisture in the sample.

The drying conditions specified were entirely arbitrary, since at higher temperatures there was danger of the decomposition of the sample and the release of free ammonia. It was possible that the moisture contents of different samples prepared under different conditions would vary. Therefore, it was necessary to choose a suitable temperature and drying time, so that the moisture contents of the samples could be compared.

Total Phosphoric Acid. The colorimetric method of Bridger, Boylan and Markey (3) was used. Although the reaction products obtained in this investigation are quite water soluble, it was necessary to boil the sample with aqua regia, just as for materials containing insoluble phosphates. The reasons for this will be discussed later.

The aqua regia-phosphoric acid solution was heated on a hot plate until the evolution of brown fumes stopped. After cooling to room temperature, it was transferred to a volumetric flask and diluted to the mark with distilled water. A suitable aliquot of the solution, containing approximately two mg of P_2O_5 was pipetted directly into a 100 ml volumetric

flask, and 25 ml of standard color solution was added. The resulting solution was diluted with distilled water to volume. The concentration of P_2O_5 in this solution was determined by measuring the transmittance of light of 420 millimicrons in a Lumetron Photoelectric Colorimeter, model 402-E, using a previously determined calibration table. This method is based on the formation of a yellow colored ammonium phosphomolybdevanadate complex which is directly proportional to the concentration of phosphoric acid present in the aliquot.

$$\% P_2O_5 = \frac{\text{mg } P_2O_5}{100 \text{ ml}} \times \frac{\text{dilution}}{\text{aliquot}} \times \frac{100}{\text{wt. sample (gram)} \times 10^3}$$

Nitrogen Determination. The nitrogen content of fertilizers may be present in the reduced or oxidized form. If nitrogen is present in the reduced form, either as protein nitrogen or ammonium salts, it may be determined by the ordinary Kjeldahl method. If the nitrogen is present in the oxidized form as nitrate nitrogen, it must first be converted to the reduced form before it can be determined by the Kjeldahl procedure.

(A) Ammoniacal Nitrogen.

The principle and procedure for the determination of ammoniacal nitrogen are identical to that of protein analysis. The Association of Official Agricultural Chemists Official Methods of Analysis, Method 2.22, (2) were used for this determination. A sample of one gram was placed in a dry Kjeldahl flask. 100 ml of distilled water were poured in to dissolve it completely. A few pieces of granulated zinc or pumic stone were added to the distillation flask to prevent bumping. Sufficient NaOH solution was added to make the solution strongly alkaline (50 ml of 0.5 N NaOH).

Then 50 ml of standard 0.1 N HCl were measured into a 500 ml Erlenmeyer receiver flask. Three to five drops of methyl red indicator were added. The flask was heated, and the distillation was continued until about two-thirds of the liquid in the flask distilled over. If the contents of the receiver became alkaline during the process of distillation, an added measured volume of the standard 0.1 N HCl was pipetted into the receiving flask. During the distillation, free ammonia was driven off to neutralize the acid. The excess acid in the solution was titrated with 0.1 N NaOH solution. The percentage of ammoniacal nitrogen was then calculated from:

$$\frac{(\text{CC } 0.1 \text{ N HCl}) - (\text{CC } 0.1 \text{ N NaOH}) \times 0.0014 \times 100}{\text{Weight of sample in grams}}$$

(B) Total Nitrogen.

Total nitrogen (including both ammoniacal and nitrate nitrogen) was determined by the Chemical Service Laboratory of Kansas State University by the modified Gunning method recommended by the Association of Official Agricultural Chemists, Method 2.26, (2).

Water Softening Test. Many phosphate compounds possess the ability to bind calcium ions by the formation of a soluble complex. The materials produced in this research were tested for this ability by the following procedure.

When a few drops of a calcium ion solution were added to an aqueous solution of these reaction products, a white precipitate formed at the point of entry. Upon shaking this precipitate dissolved in the solution to form a complex ion. By continuing the addition of a few drops of calcium ion solution, and then shaking until the first appearance of a permanent turbidity of the solution, the calcium holding ability of the

material was determined. This phenomenon occurred only under the presence of an excess of calcium ion which formed a sparingly soluble calcium salt of the complex. The determination of this effect was carried out using the Lumetron Colorimeter as a turbidity meter. In making the tests 0.5 to 1 gram of moisture-free sample was weighed out and dissolved in an amount of water calculated to give a concentration of 16 grams per liter. Before the titration, the solution was made alkaline to phenolphthalein with 0.1 N NaOH. If the solution did not become clear it was brought to a boil for a short time. The calcium ions were added by drops of 0.5 N calcium chloride solution (55.5 grams CaCl_2 per liter) from a 5 ml micro burette graduated in 0.01 ml. The end point was determined easily by watching the rapid drop of the light transmission reading in the colorimeter since this indicated the turbidity of the solution.

EXPERIMENTAL RESULTS

Efforts were made to collect the reaction products by other than electrostatic means at first. Various arrangements of filters and filter bags, using glass cloth, proved totally ineffective. Cyclone type collectors also were of no value. Some material was collected by a device composed of nested screens through which the gases passed. The capacity of such a collector was too low to be of much value, and the fraction collected was also low. However enough material was collected to analyze for N and P_2O_5 . The results showed 13 to 14 per cent nitrogen and 60 to 70 per cent P_2O_5 . Further the product appeared stable and not very hygroscopic. These results were sufficiently encouraging that arrangements were made for leasing an electrostatic precipitator from the Research-Cottrell Corporation.

After the electrostatic precipitator was installed, a series of ten runs were made under various reaction conditions. A white fluffy flour-like material was obtained as the reaction product except in Run No. 3 in which the product came from the precipitator as a hygroscopic, sticky, semi-solid material.

The reaction conditions are tabulated in Table 1. The chemical analyses of the products are given in Table 2.

Table 1. Experimental conditions.

| Run No. | Phosphorus Rate, g atoms/min | Air Rate, g moles/min | Ammonia Rate, g moles/min | Water Rate, g moles/min | Temperature in zone, °C Combustion : Reaction | | Running Time min |
|---------|---------------------------------|--------------------------|------------------------------|----------------------------|--|-----|---------------------|
| 1 | 0.271 | 27.81 | 0.892 | 0 | 320 | 280 | 6 |
| 2 | 0.271 | 27.81 | 0.634 | 0 | 320 | 250 | 6 |
| 3 | 0.271 | 27.81 | 0.436 | 0 | 438 | 402 | 5 |
| 4 | 0.271 | 27.81 | 1.031 | 0 | 380 | 314 | 5 |
| 5 | 0.271 | 27.81 | 0.892 | 0 | 320 | 267 | 5 |
| 6 | 0.271 | 27.81 | 0.892 | 0 | 286 | 227 | 7 |
| 7 | 0.271 | 55.62 | 0.892 | 0 | 95 | 95 | 5 |
| 8 | 0.271 | 55.62 | 1.308 | 0 | 180 | 174 | 5 |
| 9 | 0.165 | 55.62 | 0.892 | 0 | 100 | 100 | 5 |
| 10 | 0.271 | 55.62 | 0.892 | 0.666 | 197 | 177 | 5 |

Table 2. Analysis of products. All analyses are reported on the as-received basis.

| Run No. | Moisture, % | P ₂ O ₅ , % | Nitrogen | | Ca holding power ml 0.5 N CaCl ₂ /gm | Physical Characteristics |
|---------|--------------|-----------------------------------|--------------|---------|--|--------------------------------------|
| | | | Ammoniacal % | Total % | | |
| 1 | 1.82 | 67.8 | 13.3 | 13.5 | 8.26 | white flour, free-flowing |
| 2 | * | 68.7 | 10.7 | 12.3 | 5.20 | hygroscopic |
| 3 | not analyzed | | | | | sticky, semi-solid, very hygroscopic |
| 4 | 4.72 | 66.8 | 14.0 | 14.3 | 7.45 | white flour |
| 5 | 1.52 | 66.6 | 13.3 | 14.1 | 6.71 | white flour, free-flowing |
| 6 | 2.76 | 66.6 | 13.5 | 14.4 | 6.21 | white flour, free-flowing |
| 7 | 2.46 | 63.6 | 13.1 | 14.2 | 6.47 | white granules, free-flowing |
| 8 | 5.00 | 61.1 | 15.6 | 15.7 | 5.90 | white hard chips |
| 9 | 3.12 | 63.4 | 14.0 | 14.2 | 7.10 | white flour, free-flowing |
| 10 | 5.22 | 63.1 | 14.5 | 14.6 | 5.67 | white flour, free-flowing |

* Gained weight in dryer.

DISCUSSION OF RESULTS

The effect of the $\text{NH}_3/\text{P}_2\text{O}_5$ ratio on the reaction products was quite marked. In the first three runs this ratio (molar basis) was 6.6, 4.7, and 3.3. The first ratio appeared to be about the lowest practical value under the conditions of these tests. At a ratio of 4.7 (run 2) the product was very hygroscopic, indicating the presence of unreacted P_2O_5 . In the next run, where the $\text{NH}_3/\text{P}_2\text{O}_5$ ratio was 3.3, the product absorbed so much water in the precipitator that it was almost completely dissolved before any of it could be recovered.

In run 4 the $\text{NH}_3/\text{P}_2\text{O}_5$ ratio was 7.64; in run 8 it was 9.69, and in run 9 it was 10.74. A trend toward increased nitrogen and lower P_2O_5 contents in the products accompanies the increase in $\text{NH}_3/\text{P}_2\text{O}_5$ ratio in the reactants.

Increasing the air flow rate (runs 7, 8, 9, and 10) tended to lower the temperatures in the reactors but probably had little other effect. None of the temperatures reached the level at which NH_3 is appreciably decomposed into N_2 and H_2 . There is some indication that the increased dilution of the gases affected the reaction, since run 9, where the phosphorus rate was lowered gave a somewhat lower % nitrogen than run 8, even though the $\text{NH}_3/\text{P}_2\text{O}_5$ ratio in the reactants was higher for run 9.

The addition of more water (as steam) to the reaction mass, as was done in run 10, appeared to have little effect. Water is required in the formation of many phosphates. However the compressed air used for combustion was not dry and there may have been enough water present from this source to satisfy these requirements.

Most of the nitrogen was present as ammoniacal nitrogen, that is, it was released by heating an alkaline solution of the product. However there was a consistently larger total nitrogen content than ammoniacal nitrogen. This difference may mean that a small amount of the nitrogen was present in some form other than ammoniacal.

No effort was made to identify the actual compounds in the products obtained. However it is interesting to compare the nitrogen and phosphorus pentoxide contents of the products with those of known ammonium phosphate materials. These are given in Table 3. The compositions of the products approximate that of diammonium pyrophosphate most closely.

All of the products dissolved readily in water. When solutions of the products were used for the colorimetric determination of P_2O_5 , reasonable and accurate results could not be obtained. Similar experiences occurred when the AOAC standard volumetric method, in which the phosphate is precipitated as a complex ammonium phosphomolybdate, was used. However, when the sample was treated by the AOAC standard extraction method for insoluble phosphates, which involves boiling in aqua regia, the results were as expected and the accuracy much improved. This might have been caused by the presence of phosphates in the form of polymer chains, or in lower oxidation states than the common five valent form of phosphorus.

The water softening ability of these products was quite good compared with the commercial phosphates used for this purpose. Fischer (5) reports that Calgon ($NaPO_3$) held 4.9 ml and sodium hexametaphosphate, $(NaPO_3)_6$, held 6.4 ml of 0.5 N $CaCl_2$ solution per gram.

Table 3. Composition of ammonium phosphate compounds.

| Compound | Formula | Nitrogen, % | P ₂ O ₅ , % |
|------------------------------|--|-------------|-----------------------------------|
| Ammonium metaphosphate | NH ₄ PO ₃ | 14.43 | 73.18 |
| Mono-ammonium orthophosphate | NH ₄ H ₂ PO ₄ | 12.17 | 61.70 |
| Di-ammonium orthophosphate | (NH ₄) ₂ HPO ₄ | 21.20 | 53.74 |
| Mono-ammonium pyrophosphate | NH ₄ H ₃ P ₂ O ₇ | 7.10 | 72.10 |
| Di-ammonium pyrophosphate | (NH ₄) ₂ H ₂ P ₂ O ₇ | 13.20 | 67.00 |

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STUDIES ON THE GAS PHASE REACTION FOR THE PRODUCTION OF
AMMONIUM PHOSPHATE

by

JIH-MING WANG

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AN ABSTRACT OF A THESIS

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No industrial process exists for the vapor phase production of ammonium phosphates, though general laboratory investigations of the process have been made. The purpose of this work was to determine the types of compounds produced, the kind of collection equipment needed and the best operating conditions for such a process.

A reactor consisting of a 7-foot length of 2-inch stainless steel pipe was built. Elemental phosphorus was melted in a closed vessel consisting of a 14-inch length of stainless steel pipe. Watered, metered through a rotameter, entered the top of this vessel, displacing the molten phosphorus out of the bottom. From there it was conducted by a stainless steel tube to the reactor.

In the reactor the phosphorus was burned by a compressed air blast. The combustion products were mixed with ammonia gas and water vapor. The resulting smoke-like product was then collected.

Several types of collection equipment were tried, but the only successful one was an electrostatic precipitator obtained from the Research-Cottrell Corporation.

The products obtained were white, flour-like, and in some cases, too hygroscopic for fertilizer use. Considerable variation in physical characteristics occurred, depending largely on the ratio of ammonia to P_2O_5 in the reacting mixture.

The nitrogen and phosphorus pentoxide contents of the products were determined by chemical analysis. They generally contained about 14 to 15 per cent nitrogen and 60 to 70 per cent P_2O_5 . They were quite soluble in water, but some indication of polymerization into long chains was obtained from their analytical behavior. The products also showed

at least as much ability to hold calcium ions in soluble complexes as sodium hexametaphosphate, and therefore show promise as water softening agents.