RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

January 1971

U. D. C. 546.185+631.893.12:546.185-326

Polyphosphoric Acids and Their Ammonium Salts

L.V.Kubasova

This review examines the most important results of studies in the field of the chemistry of polyphosphoric acids and their ammonium salts. The chief physicochemical properties and characteristics of these compounds are described. Particular attention is paid to the problem of the preparation of condensed ammonium phosphates by both industrial and laboratory methods. The bibliography contains 113 references.

CONTENTS

1. Introduction 1
2. Chemistry of polyphosphoric acids 1
3. Chemistry and technology of dehydrated ammonium phosphates 4

1. INTRODUCTION

Ammonium phosphates are of considerable scientific and practical importance. Since they are compounds containing two of the most important plant nutrient elements—nitrogen and phosphorus—the various ammonium ortho-, pyro-, poly-, and metaphosphates can be used as nitrogen–phosphorus fertilisers, and some can be used as feedstuffs in animal husbandry and as technical salts. With respect to the total concentration of nutrient elements, the poly- and metaphosphates are more concentrated than the salts of orthophosphoric acid—monoammonium and diammonium phosphates. Agricultural-chemical experiments have shown that the phosphorus and nitrogen are just as effective in ammonium polyphosphates as in other water-soluble fertilisers. The high concentration of nutrients gives the polyphosphates a number of economic and agricultural-technical advantages and provides promising possibilities for their utilisation as highly effective concentrated fertilisers, but the technology of these compounds has been insufficiently developed. The extensive development of the electrothermal production of phosphorus and "thermal" phosphoric acids, and also the production of polyphosphoric acids by the evaporation of "extraction" phosphoric acid, are raising the problem of the conversion of these materials into various forms of concentrated fertilisers and technical salts.

Despite the urgency of the problem, published data on the chemistry and technology of dehydrated ammonium phosphates have not been reviewed. The present review therefore deals with the most important results of the studies of recent years in the field of the preparation and study of the properties of ammonium poly- and metaphosphates. The problems of the structural chemistry of the phosphates are not examined in detail, since this subject has been dealt with in depth in the monograph by van Wazer[1] and in reviews by Khodakov[2], Thilo[3], Britske and coworkers[4], and others.

2. CHEMISTRY OF POLYPHOSPHORIC ACIDS

As early as 1910, Balareff[5] noted that in the two-component $H_2O-P_2O_5$ system in the range of high concentrations of phosphorus(V) oxide (>72.4%), solutions consisting of a mixture of various phosphoric acids begin to form. This was one of the first suggestions that in this concentration range the 100% orthophosphoric acid formed does

not simply mix with the excess of phosphorus(V) oxide, but that a large quantity of other condensed forms of phosphate anions is gradually formed in the solution.

After the establishment of the existence of a large number of polymeric phosphates, the attention of research workers was drawn to the development of analytical methods for their separation and quantitative determination in the presence of one another. It was established that classical analytical methods based on precipitation make it possible to separate only the first three members of the homologous series of polyphosphates[6-8]. The concentration of all other polyphosphates was determined from the difference between the total concentration of phosphorus in the phosphate mixture and the phosphorus present in the ortho-, pyro-, and tripolyphosphates. This was attributed to the fact that the polymeric phosphate homologues have extremely similar chemical properties and tend to undergo hydrolysis to orthophosphate, so that attempts to separate them by precipitation are unsuccessful.

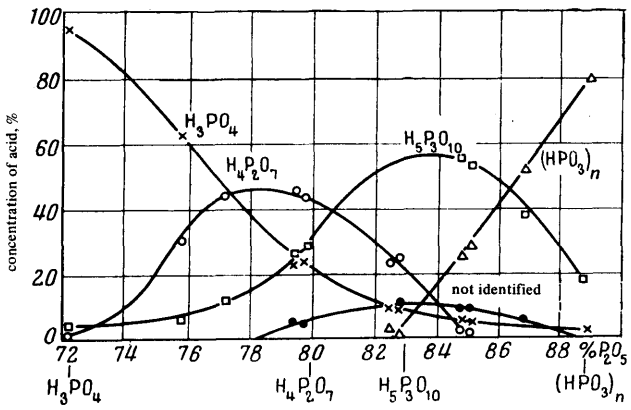


Figure 1. Composition of concentrated phosphoric acids.

Using the available analytical methods, Durgin and coworkers[9] established that phosphoric acids at high concentrations consist of mixtures of ortho-, pyro-, tripoly-, and other acids with different degrees of condensation. Later, Bell[10] detected regular features in the dependence of the production of a given phosphoric acid on the concentration of phosphorus(V) oxide in the solution (Fig. 1), namely that at concentrations in the range 72.4–85% P_2O_5 the solution always contains ortho- and pyrophosphoric acids, and in the range 72.4–88.7% P_2O_5 it also contains tripolyphosphoric acid $H_5P_3O_{10}$ in addition to these two acids. At a concentration greater than 83%, metaphosphoric acid appears in the polymeric form $(HPO_3)_n$.

Paper chromatography[11-15] has proved more successful for the separation of polyphosphate chains. Using this method, Huhti and Gartaganis[16] studied the compositions of phosphoric acids in the range 68.8–86.3% P_2O_5 and gave quantitative information on the concentration of phosphoric acids with different degrees of polymerisation in the mixture (Table 1). Unfortunately, even this most accurate method of polyphosphate analysis does not yet make it possible to separate polyphosphoric acids containing more than nine phosphorus atoms in the chain, so that the compositions of the acids with ratio $H_2O/P_2O_5 < 1.5$ have not yet been fully established. An interesting feature is that the author cited confirmed the previously noted observation[17] that liquid phosphoric acid with the theoretical composition of pure orthophosphoric acid (72.4% P_2O_5) contains 12.7% pyrophosphoric acid, the first detectable quantities of which begin to appear at 68.9% P_2O_5, and the composition of 100% orthophosphoric acid is achieved only on crystallisation.

Simon[18] considers that the rearrangement leading to partial condensation with the formation of free water and pyrophosphoric acid according to the equation

$$3H_3PO_4 \rightleftarrows H_4P_2O_7 + [H_3O]^+ + [H_2PO_4]^-,$$

takes place as a result of interaction within the three-dimensional structure and is associated with the presence of a large number of covalent bonds between hydrogen and oxygen atoms.

Table 1. Compositions of liquid polyphosphoric acids (according to Huhti and Gartaganis[16]).

Total P_2O_5 concentration	Ortho-	Pyro-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	$(HPO_3)_n$
68.80	100	—	—	—	—	—	—	—	—	—
69.81	97.85	2.15	—	—	—	—	—	—	—	—
74.26	67.78	29.54	2.67	—	—	—	—	—	—	—
75.97	48.93	41.76	8.23	0.08	—	—	—	—	—	—
78.02	26.91	49.30	16.85	5.33	1.60	—	—	—	—	—
79.45	16.73	43.29	22.09	10.69	4.48	1.92	0.80	—	—	—
81.60	8.06	27.01	22.28	16.99	11.00	5.78	3.72	2.31	1.55	1.28
86.26	1.54	2.97	3.31	5.16	5.32	5.54	3.51	3.30	3.30	66.03

At the same time, studies of liquid phosphoric acids indicated that a definite molar ratio H_2O/P_2O_5 always corresponds to the same molar composition of the solution, which consists of a mixture of phosphoric acids with different degrees of condensation. This suggested that a given liquid polyphosphoric acid molecular composition expresses an equilibrium state between different structural units, molecules and molecular ions, which in the time taken for equilibrium to be established may break down and be re-formed repeatedly. There are many examples in organic chemistry of the rearrangement of molecular structures. This phenomenon for various processes has been studied in detail from the chemical viewpoint; in addition, a mathematical treatment of the molecular weight distribution in the intermediate compounds formed has been carried out[19] and has found extensive application for the description of unionised molecules as the Flory distribution function.

van Wazer and coworkers, following Flory, extended the theory of rearrangement to polyelectrolytes, that is ionised molecules such as those of the polyphosphoric acids, and derived an equation which makes it possible, for any given molar ratio H_2O/P_2O_5, to calculate the distribution of chains of different length[20]. It should be noted that recent work has shown that it is possible to carry out a more accurate quantitative analysis of polyphosphate compounds by means of computers.

Of the large numbers of known phosphoric acids, only a few have been identified and isolated in crystalline form. These are orthophosphoric acid hemihydrate ($H_3PO_4 \cdot 0.5H_2O$) and orthophosphoric (H_3PO_4), pyrophosphoric ($H_4P_2O_7$), and tetraphosphoric ($H_6P_4O_{13}$) acids. Other polyphosphoric acids have been obtained in the form of mixtures of acids

with different degrees of condensation, and form a series of compounds ranging from syrupy liquids, which crystallise slowly when kept, to amorphous glasses. The Americans Striplin and coworkers[21] of the TVA established the range of concentrations (75–76% P_2O_5) in which polyphosphoric acids are always produced in the form of syrupy liquids and do not crystallise on prolonged storage; in their opinion, this is due to the existence of a simple eutectic with the neighbouring region of the solutions, which have a strong tendency to undergo supercooling.

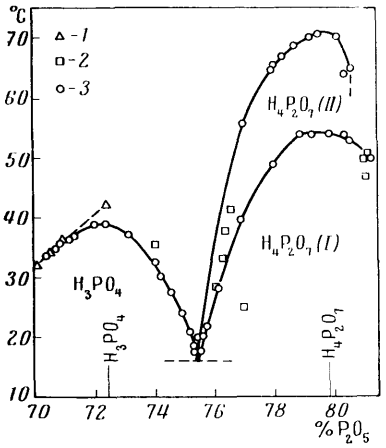


Figure 2. Fusion diagram of the $H_3PO_4-H_4P_2O_7$ system according to Refs. 23 (*1*), 24 (*2*), and 22 (*3*).

This suggestion was later confirmed by their colleague Wakefield and coworkers[22] in a study of phase changes in the $H_3PO_4-H_4P_2O_7$ system. The determination of the melting points of these acids, and the diagram constructed by the authors cited on the basis of the results obtained, show clearly the formation of a eutectic (16°) at a concentration of 75.4% P_2O_5 in phosphoric acid (Fig. 2). Moreover, the authors cited established the existence of two crystalline forms of pyrophosphoric acid, denoted (I) and (II). The ordinary metastable form (I) melts at 54.3°; the second form (II), the existence of which was confirmed by X-ray diffraction studies, melts at a higher temperature (71.5°). This form can be obtained by gradually heating the acid in form (I) above 54°, without stirring. All the acid, with the exception of a few crystals, melts, but further increase in temperature (from 60° to melting point) leads to the opposite phenomenon—all the liquid phase solidifies. The pyrophosphoric acid (II) obtained in this way is stable at room temperature. Transformation of one form of pyrophosphoric acid into the other in the solid phase was not observed. These results indicate that the melting point of 61° for pyrophosphoric acid, established in 1902 by Giran[25] and generally accepted since then reflects the melting point of a mixture of its two modifications.

In parallel with the study of the chemical compositions of polyphosphoric acids, a number of authors have determined the physical properties of these compounds. Particular attention has been paid to the study of such physicochemical characteristics as density and viscosity[9,26], a knowledge of which is very important for the industrial development of polyphosphoric acid production.

The experimental data on the density of thermal phosphoric acids over a wide range of concentrations have been treated mathematically and represented in the form of the equation given below, which makes it possible to find the temperature dependence of the density for acids at different concentrations

$$d = (0.7102 + 0.1617c) - (11.7 \cdot 10^{-4} - 6.00 \cdot 10^{-6}c)t,$$

where d is the density, g ml^{-1}; c the concentration (wt. % P_2O_5); and t the temperature, °C.

Workers from Monsanto[27] recommend a slightly simplified form of the equation for the concentration dependence of the density of the condensed acids

$$d = 0.0167(\%P_2O_5) + 0.66$$

for concentrations of phosphorus(V) oxide in the acid from 50% to 95%.

The viscosity of polyphosphoric acids was determined by Durgin and coworkers[9] in the range 71.8–77.1% P_2O_5 and by Kondratenko and Fedorchenko[28] in the range 65.2–74.6% P_2O_5. The results made it possible to establish the temperature dependence of the viscosity for a wide range of polyphosphoric acids as far as the azeotropic composition containing 92.4% P_2O_5.

Similar studies of the physicochemical properties of polyphosphoric acids obtained by the extraction method were carried out by Mal'tseva and coworkers[29,30], who were able to determine a number of thermochemical constants characterising the dilution of polyphosphoric acids; this is of considerable importance in the technology of polyphosphoric acids.

The industrial production of highly concentrated phosphoric acids is now carried out on the basis of the electrothermal process for the preparation of phosphorus and its oxidation, and on the basis of the production of extraction phosphoric acid.

Despite the fact that vacuum-evaporation, spraying, and other apparatus making it possible to increase the concentration of extraction phosphoric acids to 70% P_2O_5 [31-33] has been developed and introduced, the production of polyphosphoric acids by this method has not until recently found extensive industrial application. This is because the concentrated phosphoric acids obtained in this way in most instances are contaminated by traces of sulphuric acid, sesquioxides of iron and aluminium, etc.

In most instances, the direct method of preparing polyphosphoric acids in the electrothermal production of phosphorus is used. The production of polyphosphoric acid on a pilot-plant scale was first carried out by the TVA and in Japan[34,35]. The production scheme was as follows. The phosphorus(V) oxide vapour leaving the phosphorus combustion chamber was cooled to 460° and passed to an absorption tower, irrigated at 210–220° with concentrated 85% phosphoric acid. This high concentration of acid used for irrigation was necessary to obtain the maximal degree of absorption of phosphorus(V) oxide (99%). The concentration of acid leaving the tower was 87% P_2O_5. The proposed scheme required very rigorous observation of the temperature conditions of the absorption and the concentration of the absorbent. To avoid these technological difficulties, the same authors later proposed a new scheme for the production of polyphosphoric acid containing 76% P_2O_5,[20,36,37] according to which oxides of phosphorus containing small quantities of metaphosphoric acid at 600° were passed to a hydrating apparatus irrigated with water and dilute orthophosphoric acid. The resulting polyphosphoric acid was passed through a cooling channel into a

collector, and the unabsorbed phosphorus oxides in the form of a mist were trapped in an electrostatic filter or in a packed tower. Phosphoric acids at this concentration are extremely aggressive towards most metals, and the aggressive character increases considerably with increase in temperature to several hundred degrees, so that most of the apparatus (combustion chamber, hydration towers) had to be made of graphite or lined with acid-resistant brick.

Recently, the TVA has built a number of new plants for the production of polyphosphoric acid with increased concentration (~ 80% P_2O_5), [38] in which the old graphite equipment has been replaced by new stainless steel equipment.

In the Research Institute for Fertilisers and Insectofungicides, Postnikov and coworkers [39] have developed a new scheme for the preparation of thermal concentrated phosphoric acids (103–110% H_3PO_4). The authors rejected the old designs of plant with linings and changed to unlined metal equipment with water-cooled walls to remove the excess of heat and protect the metal from corrosion.

A number of authors have suggested a method involving the repeated rectification of a mixture of phosphoric acids and organic solvents to increase the concentration of these acids [40,41]. Recent work has shown that the best results are obtained by using such solvents as n-butanol, cyclopentanol, cyclohexanol, and 3-methylbutanol, which make it possible to reach a concentration of phosphorus(V) oxide in the acids equal to 77.8–93.8%. This method has not yet found extensive industrial application and is used only when necessary to prepare small quantities of concentrated polyphosphoric acid.

For preparative purposes, polyphosphoric acids can be obtained from the corresponding sodium polyphosphates by means of ion exchange resins in the H-form [42-47] or by adding phosphorus(V) oxide to pure orthophosphoric acid [16].

3. CHEMISTRY AND TECHNOLOGY OF DEHYDRATED AMMONIUM PHOSPHATES

The first papers on the chemistry of the salts of the above polyphosphoric acids appeared more than one hundred years ago. Graham [48], Fleitmann and Henneberg [49], Tammann [50], and a number of other workers developed methods of preparation and described a number of properties of polymeric phosphates of sodium and to a smaller extent potassium. Since inorganic chemical theory at that time was not well developed and sufficiently reliable analytical and physicochemical methods of study were not available, the authors cited made a number of errors in the nomenclature of the condensed phosphates, and this acted as a source of confusion and incorrect ideas regarding the structures of some of these compounds.

A systematic detailed study of the methods of preparation, properties, and structures of various oxygen compounds of phosphorus was undertaken about the middle of the twentieth century. Important work on the structural chemistry of the dehydrated phosphates and their classification and systematisation has been carried out by van Wazer, Thilo, Britske, and Khodakov and coworkers.

The large amount of physicochemical data obtained in the study of dehydrated phosphates, and a number of theoretical generalisations, have led these authors to the conclusion that there exist homologous series of phosphates, from the monomers to the higher members of the series, formed by the sharing of oxygen atoms between the structural units, each of which consists of a tetrahedral group of four oxygen atoms around a central phosphorus atom. Several different structural types can be distinguished in the polymeric phosphates, depending on the way in which the individual PO_4 tetrahedra are joined by the oxygen atoms shared by neighbouring tetrahedra, that is depending on the number of oxygen atoms corresponding to each PO_4 tetrahedron.

Polyphosphates —a homologous series of salts, the anions of which consist of PO_4 tetrahedra joined to one another by oxygen atoms in continuous chains of different length.

Metaphosphates $(MPO_3)_n$ are phosphates with anions having a ring structure.

Branched or network phosphates are compounds containing a greater or smaller number of "quaternary" phosphorus atoms, joined to other phosphorus atoms through three oxygen atoms. Van Wazer considers that there are several forms of structural block (point of branching, central and terminal groups) from which all these types of dehydrated phosphate can be constructed by different relative arrangements. By combining all these structural blocks in the most varied ways, it is possible to obtain a wide variety of hypothetical formulae for the condensed phosphates. The total number of structures formed in this way, however, does not always agree with the number actually existing, since the possibility of existence of a given structure is determined by steric factors (the strain in the P–O–P bonds, the size of the valency angles, etc.).

On the basis of a calculation of the total number of bonds in a given phosphate, van Wazer [51] proposed a method for calculating the formulae of phosphates of different structural types, according to which chain phosphates can be described by the formulae $M_{n+2}P_nO_{3n+1}$ and $M_nH_2P_nO_{3n+1}$, where n is the degree of condensation. Ring phosphates have the formula $M_nP_nO_{3n}$. As $n \to \infty$, the general formula of the chain polyphosphates $M_{n+2}P_nO_{3n+1}$ approaches that corresponding to the metaphosphate composition $(MPO_3)_n$, so that the last formula is the limiting formula for both chain and ring phosphates. Thus the term "metaphosphate", covering a wide range of polymeric phosphates with the composition $(MPO_3)_n$ with both chain and cyclic structures, still appears in the literature.

Despite the fact that various physicochemical methods for the study of polymeric compounds are now known and widely employed (paper chromatography, infrared spectroscopy, X-ray diffraction), the determination of the structures and molecular weights of various condensed phosphates presents considerable difficulty.

Nuclear magnetic resonance (NMR) has proved extremely effective for the qualitative determination of the compositions of mixtures of various phosphates and the investigation of their structures. The use of this method became possible because the resonance peaks in the NMR spectra of phosphates result from the presence, in the phosphate anions, of the so-called central and terminal groups, the concept of which was introduced by van Wazer. It has been established that a central group in a chain is equivalent to a central group in a ring, and also that terminal groups exhibit identical bond characteristics, irrespective of the chain length [52-54].

The NMR spectra of the anions of chain phosphates, given in Fig. 3, show clearly the change in the character of the spectrum with change in the ratio of terminal and central groups in the anion. Thus the spectrum of the pyrophosphate reflects the presence of only terminal

groups, whereas the spectrum of tripolyphosphate reveals a central group in addition. It can readily be seen that in the spectrum of the tripolyphosphate the peak of the terminal group is split to form a doublet, and the peak of the central group is a triplet. This is not accidental, but is related to the nature of the bonds in the terminal and central groups in the tripolyphosphate: each terminal group is joined to one central group, and each central PO_4 group to two terminal groups.

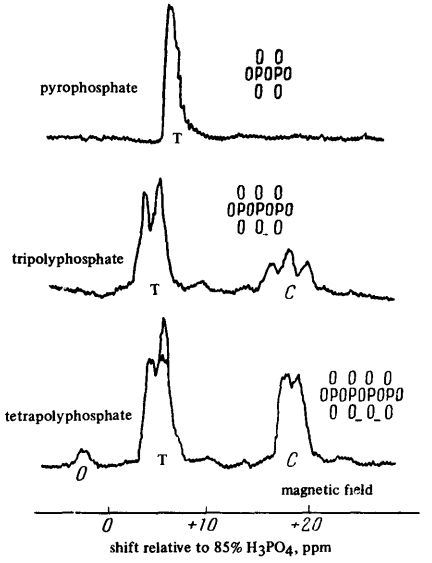


Figure 3. NMR spectra of polyphosphate anions; T—peaks due to terminal groups; C—peaks due to central groups; O—peaks due to orthophosphate.

The NMR spectrum of the tetrapolyphosphate anion in a solution of crystalline ammonium tetrapolyphosphate reflects the presence of terminal and central groups; the peaks reflecting these groups are split to form doublets, proving that this anion has a linear structure.

A characteristic feature is that the ratio of terminal to central groups can be estimated by comparing the areas under the corresponding peaks (2 : 1 for the tripolyphosphate and 2 : 2 for the tetrapolyphosphate).

All the NMR spectra of different metaphosphate specimens showed the presence of exclusively central groups, proving conclusively the original structure of the metaphosphate anions.

Unfortunately, the NMR method has not yet been sufficiently fully developed for the quantitative analytical determination of mixtures of phosphates.

The existence of "inorganic rings" with six members (trimetaphosphates) and eight members (tetrametaphosphates) has suggested the possible production of different steric configurations in these compounds, analogous to that observed in the chemistry of organic cyclic compounds (cyclohexane, decalin, etc.).

The most detailed studies from the viewpoint of stereochemistry have been made for only two ammonium salts, the trimetaphosphate $(NH_4)_3P_3O_9$ and the tetrametaphosphate $(NH_4)_4P_2O_{12}$, which are comparatively stable in aqueous solution and do not undergo immediate hydrolysis. It has been found that the molecules of these compounds can in fact exist in two different geometric configurations: the boat form (a) and the chair form (b) (Fig. 4).



Figure 4. Configuration of the molecules of ammonium tri- and tetrametaphosphates: *a*) boat form; *b*) chair form.

As a consequence of the difference in various physical and chemical properties of these geometric isomers, it is comparatively easy, by fractional crystallisation or paper chromatography, to separate their mixtures and identify each of the forms for more detailed study. Thus Romers and coworkers[55] made an X-ray diffraction study of one of the isolated isomers of ammonium tetrametaphosphate, with the chair conformation. They were able to establish the presence of regular PO_4 tetrahedra in the metaphosphate anions; the phosphorus atoms are not situated at the centres but are displaced away from the oxygen atoms common to two tetrahedra. The authors cited attributed this to the influence of hydrogen bonds between the unshared oxygen atoms of the PO_4 groups and the nitrogen atoms of the ammonium ions. This explanation has been disputed by van Wazer, since the displacement of the phosphorus atoms may be due to the presence of negative charges on the unshared oxygen atoms as a consequence of the ionisation of the phosphate anion.

This is only one of many examples indicating that many problems of the stereochemistry of condensed phosphates are still unsolved (methods for proving spatial configurations, and their separation), and for various extremely interesting problems, such as the presence of a conformation or the interconversion of rings etc., there is almost no published information.

The possibility of extensive and varied applications of polymeric phosphates in the national economy has drawn the attention of research workers to not only the chemistry but also the technology of these compounds. Attempts have been made to find simpler and more rational methods for their preparation. Phosphates with polymeric compositions were first prepared not by neutralising the corresponding polyphosphoric acids but by the thermal dehydration of acid salts of orthophosphoric acid:

$$n\,MH_2PO_4 \rightarrow (n-1)\,H_2O + M_nH_2P_nO_{3n+1},$$

and for this reason they have been called dehydrated phosphates.

This comparatively simple method has found extensive application for the preparation of polyphosphates of sodium, potassium, lithium, and other elements, namely those for which the acid orthophosphates do not undergo any changes other than removal of water of constitution in the temperature range of dehydration. These compounds have been studied in most detail. (The results of studies published up to 1956 have been reviewed by van Wazer in the first volume of the monograph "Phosphorus and its Compounds".)

There is very little information on the ammonium salts of polyphosphoric acids. This is apparently due to the fact that the method of thermal dehydration, widely employed in practice for the preparation of poly- and metaphosphates, cannot be used for the ammonium salts, since with increase in temperature, ammonium hydrogen orthophosphates decompose with the liberation of ammonia before dehydration takes place.

In 1955, Thilo and Grunze[56] investigated the thermal dissociation of monoammonium phosphate in order to study the reaction products with maximal degree of dehydration. They showed that the decomposition of monoammonium phosphate on heating takes place in stages according to the reactions

$$NH_4H_2PO_4 \xrightarrow[\text{up to } 140^\circ]{-NH_3} NH_4H_2PO_4 + H_3PO_4 + NH_3$$

$$NH_4H_2PO_4 \xrightarrow[140-190^\circ]{-NH_3;\ -H_2O} (NH_4)_n H_2P_nO_{3n+1};\ (NH_4, H)_{n+2}P_nO_{3n+1}$$

$$(NH_4)_n H_2P_nO_{3n+1} \longrightarrow H_{n+2}P_nO_{3n+1}$$
$$(NH_4)_n H_2P_nO_{3n+1} \xrightarrow{200-300^\circ} (NH_4PO_3)_n$$

$$(NH_4PO_3)_n \xrightarrow[300^\circ]{-NH_3} (HPO_3)_n$$

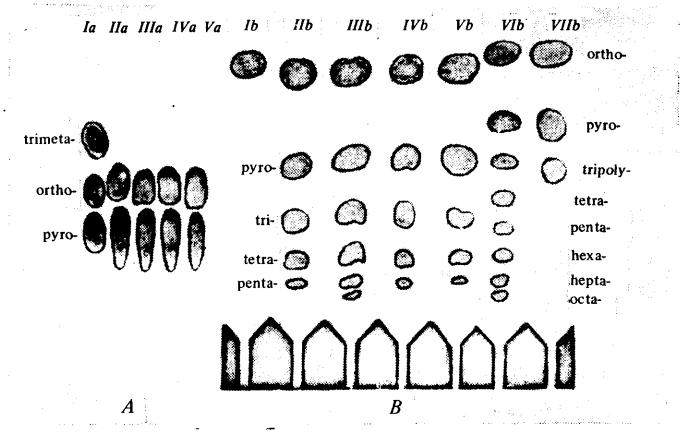


Figure 5. Paper chromatogram for the products of the dehydration of $NH_4H_2PO_4$ (*A*—chromatography in ammoniacal solution; *B*—chromatography in acid solution); *Ia*) mixture of standards (trimeta-, ortho-, and pyrophosphates), *Ib*) $NH_4H_2PO_4$ after heating for 24 h at 140°, *II*–*VII a* and *b*) products of the dehydration of $NH_4H_2PO_4$ at 150, 160, 170, 200, 230, and 250° (for 24 h).

From this it follows that the dehydration of monoammonium phosphate, which begins at ~ 140°, is accompanied by the liberation of ammonia. Using paper chromatography to analyse the dehydration products, Thilo and Grunze established that in the range 140–190° a mixture of oligophosphates with the composition $(NH_4)_nH_2P_nO_{3n+1}$, with degree of condensation n in the range 1–5, is formed. On further heating, the greater part of the mixture is converted, with loss of ammonia, into polyphosphoric acids with higher molecular weight, and a very small fraction is converted into a water-insoluble macromolecular crystalline ammonium polyphosphate (Fig. 5). Above 300°, this salt also is unstable, and decomposes with the liberation of ammonia to form polyphosphoric acid.

Analogous phenomena were observed by Japanese workers in a study of the possibility of preparing ammonium polyphosphates by the thermal degradation of acid ammonium salts of orthophosphoric acid. Unlike Thilo, Kobayashi[57] was able, not merely qualitatively, to characterise the dehydration of monoammonium phosphate at various temperatures from 175° to 300° ± 5° with heating for different periods of time (maximal duration of dehydration 25 h). Data on the ratios of pyro- and tripolyphosphates and phosphates with higher molecular weight, and also on the quantity of undehydrated orthophosphate, were obtained by ion exchange chromatography on Dowex-1-X8 resin (KCl solutions with different concentrations were used as eluant). It was established that even at 300°, dehydration is not complete, and the final product contains from 15% to 5% P_2O_5 in the ortho-form, relative to its total concentration, depending on the duration of heating. Increase in the duration of heating at any temperature leads to more complete dehydration, but the relationships for the formation of pyro- and tripolyphosphates and other dehydrated forms of phosphate are different. At 175, 200, and 225°, a general tendency for the dehydrated forms of the phosphates to increase with increase in the duration of dehydration is observed, whereas at higher temperatures (260 and 300°), at definite stages of the dehydration, the quantity of pyro- and tripolyphosphates formed reaches a maximum and then gradually decreases, with a corresponding increase in the quantity of polyphosphates with higher molecular weight.

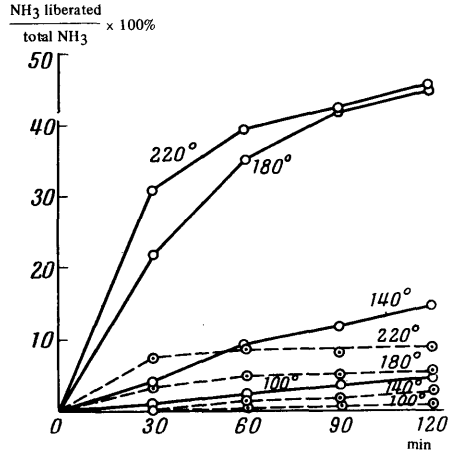


Figure 6. Dependence of the liberation of ammonia on the time for which diammonium phosphate and ammonium polyphosphate are heated at various temperatures: continuous lines—diammonium phosphate; broken line—polyphosphate.

The chemical compositions of the products show that in fact the dehydration of monoammonium orthophosphates is accompanied by appreciable loss of ammonia; the concentration of ammonia gradually decreases from 16% at 175° to 11% at 300° (heating for 25). The formation of acidic ammonium polyphosphates ($NH_4 < H$) is also confirmed by the fact that solutions of the specimens studied had an acidic reaction (pH 2.5–4.0).

It should be noted that the ammonium polyphosphates themselves decompose with the liberation of ammonia with much greater difficulty than the original salts of orthophosphoric acid[58]. This is clearly confirmed by data obtained in a study of thermal dissociation up to 220° over a period of 2 h for diammonium phosphate and ammonium polyphosphate with an average degree of condensation n = 7–8 (Fig. 6). Above 140°, diammonium hydrogen phosphate is converted into a mixture containing varying quantities of diammonium pyrophosphate and triammonium tripolyphosphate[59].

To obtain ammonium phosphates with the maximal degree of dehydration, corresponding to the chemical composition $(NH_4PO_3)_n$, Vol'fkovich and Kubasova[60] proposed a method for the thermal dehydration of ammonium hydrogen orthophosphates under a pressure of gaseous ammonia.

The use of gaseous ammonia in the dehydration made it possible to find conditions in which the pressure of ammonia vapour during the decomposition is balanced by the ammonia pressure created above the original salt, and the dehydration proceeds without the loss of ammonia (at an approximately constant molar ratio NH_3/P_2O_5), with a continuously increasing degree of dehydration, that is with a decrease in the molar ratio H_2O/P_2O_5 in the dehydration products. The greater part of the water of constitution is removed from monoammonium orthophosphate in the range 275–325°, after which the rate of dehydration decreases; the composition of the products approaches that of macromolecular polyphosphates of the type $(NH_4PO_3)_n$.

Unfortunately, the production of ammonium polyphosphates by thermal dehydration must at present be regarded as a preparative method, since all the experiments were carried out in laboratory apparatus by batch methods. The pilot-plant or industrial introduction of this method of preparation requires the development of equipment which would make possible a continuous process.

Recently, Kobayashi[61] described a study of the kinetics of formation of condensed ammonium phosphates in a continuous process involving the reaction of thermal phosphoric acid with ammonia. The experimental assembly is illustrated in Fig. 7. The starting materials (phosphoric acid and ammonia) were introduced into the first reaction vessel, which was heated by external and internal heaters to 230° or 250°, after which phosphoric acid, previously heated to 100° by heat exchange with steam leaving the reaction vessel, was introduced into the reaction vessel. Contact between the phosphoric acid and the liquid in the reaction vessel led to intensive volatilisation with the removal of a large proportion of the water, leaving a salt melt in the reaction vessel. With mixing (rate of stirring 200 rev min^{-1}) the phosphoric acid reacts with ammonia (simultaneous ammonium salt formation and dehydration), as a result of which the level of liquid in the reaction vessel increases and the product is removed continuously from the reaction vessel through an outlet.

For $(NH_4)H_2PO_4$ heated in a batch process, the rates of formation of the individual salts (r_2 for pyrophosphate, r_3 for tripolyphosphate, and r_m for the average polyphosphate) were calculated by substituting the apparent rates of formation in the reaction rate equation derived on the basis of the known mechanism of complex formation. The following values were obtained for the range 230–250°: $r_2 = 2 \times 10^{-2} - 1 \times 10^{-3}$ mole min^{-1}, $r_3 = 5 \times 10^{-3}$ mole min^{-1}, and $r_m = 1 \times 10^{-3} - 1 \times 10^{-4}$ mole min^{-1}.

The rates of the reaction between phosphoric acid and ammonia were determined from the kinetic equation applicable to continuous processes in bulk apparatus. In these experiments it was established that the concentration of condensed phosphates in the final product decreases with increase in the input of starting materials. The reaction rate increases, however. Thus for example at a reaction temperature of 250°, increase in the input of phosphoric acid by increasing the concentration from 30% to 50% (calculated as P_2O_5) increases the reaction rate from 0.385 kg h^{-1} $litre^{-1}$ to 0.651 kg h^{-1} $litre^{-1}$.

The products contained 10–12% nitrogen and 62–67% P_2O_5 and had an acidic reaction. For this reason, the treatment with ammonia was repeated. The condensed phosphates obtained in this way contained 13–15% nitrogen and 65% P_2O_5. The degree of conversion of $(NH_4)H_2PO_4$ into $(NH_4 + H)_{n+2}P_nO_{3n+1}$ (where n = 2–10) was 60–80%.

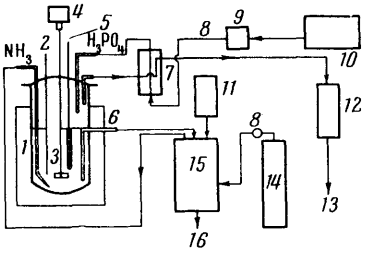


Figure 7. Diagram of the laboratory apparatus for the preparation of condensed ammonium phosphates[61]: *1*) external heater; *2*) thermistor; *3*) first reaction vessel; *4*) motor with stirrer; *5*) heating element; *6*) removal of product; *7*) heat exchanger; *8*) flow meter; *9*) pump; *10*) phosphoric acid tank; *11*) vessel for added salts; *12*) cooler; *13*) water; *14*) ammonia cylinder; *15*) second reaction vessel for repeated treatment with ammonia; *16*) final product.

The experiments showed that the ammonium polyphosphate obtained can be mixed with a number of salts containing various nutrient elements, for example with potassium chloride during the repetition of the treatment with ammonia, and this is of interest for the preparation of complex fertilisers.

Various dehydrated ammonium phosphates can also be prepared by ion exchange from solutions of the polymeric phosphates of other cations, followed by treatment of the polyphosphoric acid solutions with ammonia and precipitation of the crystalline salts with ethanol or acetone[62,63].

A number of papers describing the properties of condensed ammonium phosphates, prepared by ion exchange, have been published[64,65]. Unfortunately, some contain inaccurate data, since they describe not the pure salts but their mixtures. Ammonium pyro- and tripolyphosphates have been most fully characterised in a review by Frazier[66], who described the methods of preparation and the crystallographic properties of six pyrophosphates: $(NH_4)_2H_2P_2O_7$ (monoclinic and orthorhombic), $(NH_4)_3HP_2O_7$, $(NH_4)_3HP_2O_7.H_2O$, $(NH_4)_4P_2O_7$, $(NH_4)_4P_2O_7.H_2O$, and six tripolyphosphates: $(NH_4)_3H_2P_3O_{10}$, $(NH_4)_3H_2P_3O_{10}.H_2O$, $(NH_4)_4HP_3O_{10}$, $(NH_4)_9H(P_3O_{10})_2.2H_2O$, $(NH_4)_5P_3O_{10}.H_2O$, and $(NH_4)_5P_3O_{10}.2H_2O$. All these salts were prepared from recrystallised reagents or obtained as solid phases in the

determination of solubility according to Farr and Fleming[67] in the $NH_3-H_4P_2O_7-H_2O$ and $NH_3-H_5P_3O_{10}-H_2O$ systems. To obtain reliable results, the authors cited prepared the original condensed ammonium phosphates by three methods. The passage of solutions of $Na_4P_2O_7$ or $Na_5P_3O_{10}$ through Amberlite IR-120 resin which had been treated with acid gave solutions of the corresponding acids, which were immediately treated with ammonia and evaporated in a vacuum. To prevent hydrolysis, all these operations were carried out below 10°.

Ammonium tripolyphosphates were prepared by fractional crystallisation of the products obtained by treating thermal superphosphoric acid (79–82% P_2O_5) with ammonia. $(NH_4)_5P_3O_{10}\cdot H_2O$ was purified by recrystallising eight times. Other tripolyphosphates were obtained by lowering the pH of solutions of this salt with Amberlite IR-120 resin and then treating the eluate with ethanol. The salt frequently separated in the form of an oily liquid; a seed crystal was added to bring about crystallisation.

Ammonium pyrophosphate $(NH_4)_4P_2O_7$ was prepared by treating aqueous solutions or suspensions of calcium ammonium pyrophosphates with ammonium fluoride. This salt was recrystallised and used for the preparation of more acidic ammonium pyrophosphates.

A recently published paper by French workers[68] on the isolation of a new ammonium salt with mixed orthophosphate and pyrophosphate anions $(NH_4)_2H_5(PO_4,P_2O_7)$, with melting point 93° ± 1°, is of interest. According to the authors cited, this acidic ammonium phosphate is a new compound and should not be regarded as an intermediate product of the thermal dehydration of the orthophosphate with formation of the pyrophosphate.

Frazier[66], and later other workers[69], paid particular attention to the problems of the stability of ammonium pyro- and tripolyphosphates; this is of direct interest in the study of the possibility of using condensed ammonium phosphates as highly concentrated liquid and solid nitrogen-phosphorus fertilisers. Thus it has been established that tetrasubstituted ammonium pyrophosphate, unlike the analogous potassium and lithium salts, does not condense in the presence of acetic anhydride at room temperature, but at higher temperatures it forms a mixture of linear phosphates[70]. The solubility of ammonium pyro- and tripolyphosphates and the phase changes in the $NH_3-H_4P_2O_7-H_2O$ and $NH_3-H_5P_3O_{10}-H_2O$ systems were studied by Farr and coworkers[71].

Ion exchange has been used to isolate not only ammonium polyphosphates with a chain structure, but also ammonium salts with the metaphosphate composition containing phosphate ions with ring structures—ammonium trimeta- and tetrametaphosphates; this is attributed to the stability of trimeta- and tetrametaphosphoric acids in aqueous solutions. It has been established[73] that ammonium trimetaphosphate is stable as far as 100°, but on further heating at 120–180° it undergoes hydrolysis, absorbing moisture from the atmosphere, and is converted into a mixture of acidic "oligophosphates" with the composition $(NH_4)_nH_2P_nO_{3n+1}$. Above 180° these compounds also decompose with the liberation of ammonia, with the formation of polyphosphoric acids containing traces of macromolecular ammonium polyphosphate.

Chromatographic analysis (Fig. 8) showed that the thermal dissociation of ammonium tetrametaphosphate takes place analogously only if the salt is heated gradually over a prolonged time interval. If the heating is rapid, over a period of 2–3 h, a macromolecular crystalline ammonium polyphosphate containing an anion with a chain structure is formed.

The properties of crystalline ammonium polyphosphate with the composition $(NH_4)_{n+2}P_nO_{3n+1}$, where $n \sim 50$ or more, have been described[66]. This salt was prepared from the product obtained by treating superphosphoric acid (83–84% P_2O_5) with ammonia, by crystallisation as the transparent ammonium polyphosphate gel dissolved. The crystals, when washed with acetone and dried in air, are stable at room temperature and remain crystallographically unchanged when heated at 105° for 48 h. This polyphosphate does not show a great similarity to Madrell's or Kurrol's salts as far as optical properties are concerned. Its infrared spectrum is similar to that of Kurrol's salt and is quite unlike that of metaphosphates containing phosphate anions with a cyclic structure.

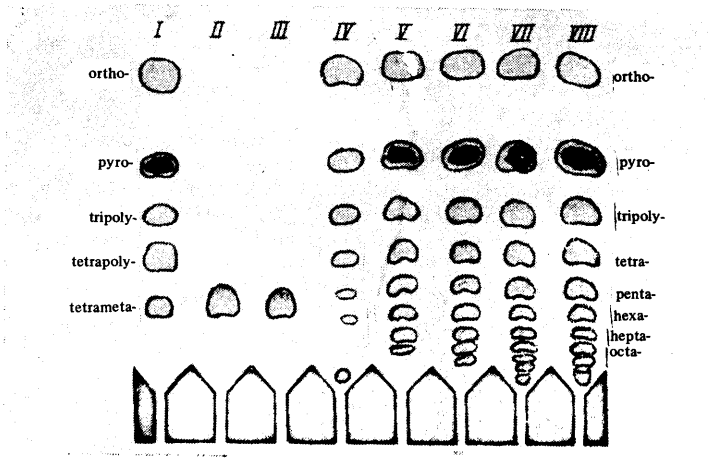
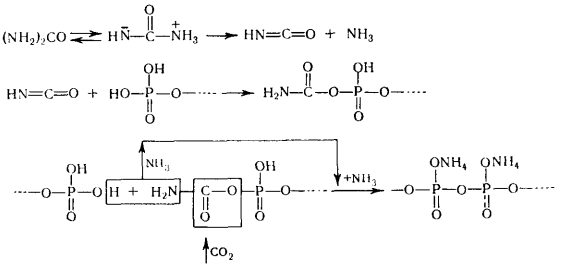


Figure 8. Paper chromatogram for the products obtained by heating ammonium tetrametaphosphate. Bands: *I*) standards (ortho-, pyro-, tripoly-, tetrapoly-, and tetrametaphosphates); *II*) $(NH_4)_4P_4O_{12}$; *III – VIII*) products obtained by heating $(NH_4)_4P_4O_{12}$ for 24 h at 100, 150, 200, 250, and 280°.

In recent years a number of papers reflecting the search for new methods for the preparation of ammonium polyphosphates from various phosphoric acids, including the use of urea as nitrogen-containing reagent, have been published. Phosphoric acids react with urea in solution and in the melt to give complex compounds—urea phosphates $(NH_2)_2CO.H_3PO_4$.[74–76] Japanese workers have established that reaction between phosphoric acid and urea begins at temperatures close to the decomposition temperature of urea with the formation of ammonium polyphosphate[77–79]. The authors cited paid particular attention to the influence of temperature, the concentration of the original phosphoric acids, and the quantitative component ratios, on the composition and properties of the compounds obtained. As original phosphoric acids they chose liquid polyphosphoric acids, containing 71.2–87.8% P_2O_5. The quantities of urea taken for the reaction were calculated from the given ratios $(NH_2)_2CO:P_2O_5$, equal to 1–4. It was found that the reaction of the polyphosphoric acids with urea in the ratio $P_2O_5:(NH_2)_2CO = 1:2$ even at 80° gives a sufficiently high yield of ammonium polyphosphates, although part of the urea remains unreacted (up to 14.6%

with acid containing 71.2% P_2O_5 and about 4% with acid containing 87.8% P_2O_5).

The reaction proceeds to the greatest extent at 140°–160°. The isocyanuric acid liberated, in the opinion of the authors cited, indicates that the following reaction mechanism is most probable:



The small quantities of isocyanuric acid present can be readily removed by filtration, and the ammonium polyphosphate formed is removed from the solution by adding ethanol. The results in Table 2 show that the quantity of unreacted urea and isocyanuric acid liberated depends chiefly on the quantitative original component ratios.

Table 2. Compositions and qualitative ratios of the products of the reaction of polyphosphoric acids and urea at 140°.

Basic data on the reaction	Concn. of P_2O_5 in the original polyphosphoric acid, wt.%						
	83.0			87.6			
Starting materials							
Polyphosphoric acid, g	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Urea, g	23.4	35.1	46.8	18.5	37.0	55.5	74.6
Ratio $(NH_2)_2CO:P_2O_5$	1.3	2.0	2.6	1.0	2.0	3.0	4.0
Reaction products							
Ammonium polyphosphate							
$(NH_4)_2O$, %	26.2	26.7	27.2	20.3	26.4	27.2	27.1
P_2O_5, %	72.5	72.1	72.3	60.9	73.0	73.1	72.2
$(NH_4)_2O:P_2O_5$ molar ratio	0.98	1.01	1.03	0.91	0.93	1.02	1.03
Average chain length	14.4	17.3	14.6	16.2	26.4	17.3	16.8
pH (1% solution)	6.1	6.4	6.2	2.3	5.9	6.2	6.2
Unreacted urea, %	3.3	10.2	16.6	1.1	3.1	12.7	17.9
Isocyanuric acid, %	3.0	3.7	3.0	5.5	14.5	18.0	9.0

The condensation mechanism of formation of ammonium polyphosphates has been proved by infrared spectroscopy [80,81]. All the polyphosphates obtained in this way contained anions with a chain structure. The average length of the chains in the anions was determined by potentiometric titration of the weakly acidic terminal OH groups. The quantitative ratio of phosphate anions with different degrees of condensation was established chromatographically. Phosphoric acid (61–69% P_2O_5) gave ammonium polyphosphates with a relatively short chain, and polyphosphoric acid (80–88% P_2O_5) gave compounds with a much longer chain.

The formation of condensed phosphates when monoammonium phosphate and urea are heated together (110–120°) was established by Vol'fkovich and coworkers [82], who made a physicochemical study of the production of nitrogen–phosphorus fertilisers from polyphosphoric acids and and intermediate product of the preparation of urea.

Industrial methods for the preparation of ammonium polyphosphates are based on the treatment with ammonia, a reaction which has been well studied for orthophosphoric acid. To increase the extent of the reaction of ammonia with the polyphosphoric acids, many authors have proposed that the process be carried out, as in Soviet work, under a pressure of gaseous ammonia [83–87]. Thus Getsinger and coworkers studied the reaction of ammonia with polyphosphoric acid containing 76% P_2O_5, under an ammonia pressure of 0.7–21 atm at 170–230°.

The neutralisation was carried out in a stainless steel reaction vessel with turbine stirrer. The reaction is very exothermic, so that to prevent decomposition of the final products, some of the heat of the reaction was removed by circulating water. The ammonium polyphosphates were obtained in the molten state. To improve the physical properties and in particular to decrease the hygroscopic character of the polyphosphates, the melt was granulated. Analysis of the final products showed that they consist of a mixture of ammonium polyphosphates with different degrees of dehydration, the chief components being monoammonium orthophosphate and the neutral and acidic ammonium pyrophosphates $(NH_4)_4P_2O_7$ and $(NH_4)_3HP_2O_7.H_2O$. The composition of the products varied from 16-61-0† to 18-69-0, depending on the conditions of treatment with ammonia (temperature, pressure, and duration of interaction of the reagents).

To develop technological conditions for the production of ammonium polyphosphates, experiments were carried out on a pilot-plant assembly with thermal phosphoric acid (77% P_2O_5) and highly concentrated extraction phosphoric acid (72% P_2O_5). [88] The treatment of the phosphoric acids with gaseous ammonia was carried out in an autoclave similar to that described earlier, at an automatically controlled pressure of 1.75–2.5 atm. The ammonium polyphosphate melt removed from the reaction vessel at 190° was passed to a horizontal two-roller mixer-granulator, in which it was simultaneously cooled to 60–100°, depending on the concentration of phosphoric acid used. The final solid product contained 14–15% N and 59–61% P_2O_5 (total), of which 40–50% P_2O_5 was in the dehydrated form.

According to a patent of Hignett and Getsinger [89], ammonium polyphosphates are obtained in the form of a solidified melt from gaseous ammonia and polyphosphoric acid (74–85% P_2O_5) or concentrated extraction acid (65–75% P_2O_5) at a pressure of 0.7–7 atm and 173–196°. The product was a mixture $(NH_4 + H)_{n+2}P_nO_{3n+1}$, with n = 2–10, containing 16% N and 61% P_2O_5.

In recent years, laboratory experiments have been carried out in the USSR, in the Samoilov Fertiliser Research Institute, on the preparation of solid ammonium polyphosphate by the treatment of polyphosphoric acids with ammonia without pressure, and it has been shown that it is possible in principle to obtain a product with good physical properties [90].

The TVA has developed on the laboratory scale a two-stage process [91] for the preparation of ammonium polyphosphate from extraction phosphoric acid (containing 55% P_2O_5) by neutralisation at an elevated temperature (121–155°). To prevent solidification of the ammonium polyphosphate melt, the temperature in the second neutralisation vessel was kept at an even higher level (~ 246°). The melt, containing ~ 50% phosphate in the polyphosphate form, was transferred to a screw granulator together with the recycle. The final product contained 11–12% N and 63–59% P_2O_5.

The direct reaction of phosphorus(V) oxide with ammonia might be of interest for the preparation of ammonium phosphates with the maximal degree of dehydration.

---

† Conventional symbols for the composition of the fertilisers: 16% N; 61% P_2O_5; and 0% K_2O.

This reaction has been known for a long time and has been studied by many workers[92-96]. It has been established that, irrespective of the conditions of the reaction, the production of (P–O–P) bonds and the production of (P–NH–P) bonds in the final products are equally probable, and this leads to the formation of a mixture of nitrogen-phosphorus compounds with different compositions, such as: diamidopyrophosphoric acid $P_2O_3(NH_2)_2(OH)_2$, diammonium monoamidophosphate $P_2O_3(ONH_4)_2(NH_2)(OH)$, or the ammonium salt of a polyphosphoric acid in which the phosphorus atoms are joined not only through oxygen atoms but also through imido-groups (NH).

Thus ammonium poly- or metaphosphates have not yet been obtained in the P_2O_5–NH_3 system. The formation of dehydrated ammonium phosphates of this kind should be expected in the NH_3–P_2O_5–H_2O system.

A thermodynamic calculation by Britske and Dunaev[92] confirmed the possibility of obtaining ammonium poly- and metaphosphates in acceptable yield by the gaseous-phase reaction of phosphorus(V) oxide, ammonia, and water vapour; the formation of phosphates containing imido- and amido-groups is not excluded. The characteristics and composition of the products obtained in this ternary system depend not only on the $NH_3 : P_2O_5 : H_2O$ ratio, temperature, and duration of the interaction between the components, but also on a number of other factors, including the order in which the components are introduced.

A continuous process for the preparation of dehydrated ammonium phosphates in stages, carried out on a pilot-plant assembly by Stinson and coworkers[97], is apparently of technological interest. Phosphorus is burned in a stainless steel vessel at 370–405°. The phosphorus(V) oxide vapour produced is directed by means of a stream of dry air to a reaction vessel in which the first stage—the reaction of the phosphorus(V) oxide with gaseous ammonia—is carried out at 400–540°. Change in the temperature of the reaction within the range indicated, and the quantity of air used, had no influence on the properties of the intermediate products. These consisted of a mixture of various amido- or imido-derivatives of phosphoric acids with different degrees of dehydration. To obtain the final product with the metaphosphate composition, the second stage was carried out; this involved the treatment of the resulting mixture of intermediate products with steam in a rotating drum. This high-temperature hydrolysis leads finally to the formation of a product exhibiting good physical properties, in that it is relatively non-hygroscopic and is readily granulated. 70–75% of this product consisted of macromolecular ammonium polyphosphate $(NH_4PO_3)_n$ containing 16–19% nitrogen and 74–79% phosphorus(V) oxide. The remaining fraction of the product consisted of complex nitrogen-phosphorus compounds, the nature of which was not studied. From the equations for the reactions which may take place in the process, however:

$$P_4O_{10} + 4NH_3 = 2PN(OH)_2 + 2H_2O$$
$$PN(OH)_2 + H_2O = NH_4PO_3$$
$$PN(OH)_2 + NH_3 = PN(OH)ONH_4$$

the authors cited conclude that 10–15% consisted of $PN(OH)ONH_4$ and 10–20% of $PN(OH)_2$. Vol'fkovich and coworkers[98,99] in the Scientific Research Institute for Fertilisers and Insectofungicides and Moscow State University carried out laboratory studies on the preparation of phosphamic compounds from P_2O_5 and NH_3 in order to produce fertilisers not bound by soils.

Japanese workers[100-103] have also studied nitrogen-phosphorus compounds formed in the P_4O_{10}–NH_3 and P_4O_{10}–NH_3–H_2O systems. They established that equilibrium mixtures of low-molecular forms of ammonium polyphosphates $(NH_4 + H)_{n+2}P_nO_{3n+1}$ are obtained by the reaction of phosphorus(V) oxide with ammonia (or ammonium orthophosphate) in the presence of a small calculated quantity of water at comparatively low temperatures, up to 150–180°. Increase in temperature and the pressure of ammonia in the reaction vessel leads to the formation of condensed vitreous phosphates. Thus at 300–450° and an ammonia pressure of ~ 30 atm the composition of the reaction products is close to the metaphosphate composition: 16–18% NH_3 and 62–67% P_2O_5.

The authors cited confirmed that ammonium polyphosphates containing imido-groups are obtained when insufficient water vapour is present in the system. In this instance, increase in temperature leads to the production of vitreous forms of dehydrated phosphates, in which only 70–75% of the total nitrogen is present in the ammonium form, the remaining fraction being present as amido- or imido-groups.

The ammonium polyphosphates obtained by various methods are at present used not only as solid but also as liquid nitrogen-phosphorus fertilisers[36]. Dissolution of ammonium polyphosphate in water gives a liquid fertiliser with the composition 10-34-0, which is the same as that obtained by treating superphosphoric acid with ammonia. Thermal orthophosphoric acid, however, gives liquid nitrogen-phosphorus fertilisers with a lower concentration of nutrients (8-24-0).[104] According to Young[105], liquid fertilisers are obtained by dissolving ammonium polyphosphates in water or aqueous ammonia.

Since superphosphoric acid containing 76% P_2O_5 is a comparatively expensive product and is produced in insufficient quantities, it was proposed that liquid nitrogen-phosphorus fertilisers be produced from a mixture of acids: extraction phosphoric acid and a superphosphoric acid solution which had been treated with ammonia[106]. Moreover, the addition of polyphosphoric acid to orthophosphoric acid prevents the precipitation of impurities which usually separate when the latter is treated with ammonia. The introduction of potassium-containing components into the liquid nitrogen-phosphorus fertilisers makes it possible to obtain complex NPK-fertilisers with varied compositions[107,108].

Determination of the solubility of various dehydrated forms of ammonium phosphates has confirmed that it is possible to obtain ammonium polyphosphates in a form which is insoluble in water but soluble in ammonium citrate and citric acid solutions; this is of interest for the preparation of concentrated nitrogen-phosphorus fertilisers with different solubilities and mobilities in soil[109,110]. It was noted that structural factors play a part in the change in the solubility of the polyphosphates. Macromolecular crystalline polyphosphates were almost insoluble in water, whereas the amorphous compounds dissolved extensively and fairly rapidly in water. It was established that in the production of a given polyphosphate structure, a particularly important role is played by such factors as the stabilisation of various crystal lattices, the rearrangement of molecules, etc.[111] Sufficiently detailed theoretical studies of this problem have not yet been made, however, and the accumulated experimental data on the influence of various factors on the production of nitrogen-phosphorus polymeric compounds with a given solubility are not used in technology.

Practical disadvantages of most dehydrated ammonium phosphates as fertilisers are that the molar ratio of nitrogen to phosphorus does not correspond to the requirements of a large number of soils and agricultural crops, and also the hygroscopic nature of many of these salts. Many workers have therefore proposed that they be used in mixed

and liquid fertilisers. A number of proposals have been aimed at improving the physical properties by granulation and the introduction of conditioning additives.

The rapid development of sources of electrical energy, the increase in natural gas and petroleum resources, and the considerable progress in the field of high-temperature reactions, particularly electrothermal reactions, reactions in cyclones and plasma, etc., are enabling research workers to introduce new and more rational schemes for the production of highly concentrated phosphoric acid and macromolecular condensed phosphates [112,113]. In turn, the industrial development of thermal reactions for processing phosphates and preparing polymeric phosphates requires detailed physicochemical studies using the latest instrumental methods of analysis in order to elucidate the chemistry of the process and to determine the optimal conditions for carrying it out.

In conclusion, we may express the hope that the chemistry of polyphosphoric acids and dehydrated ammonium phosphates will attract the attention of a wider circle of research chemists, and that the results of their work will find varied application in various branches of the national economy, particularly in the field of concentrated and complex fertilisers.

REFERENCES

1. J. R. vanWazer, "Phosphorus and Its Compounds" (Translated into Russian), Vol. 1, Inostr. Lit., Moscow, 1962, pp. 330–374, 462–610.
2. Yu. V. Khodakov, Zhur. Neorg. Khim., 1, 368 (1956).
3. E. Thilo, Zhur. Prikl. Khim., 29, 1620 (1956).
4. E. V. Britske, Trudy Nauch. Inst. Udobrenii, No. 59 (1929).
5. D. Balareff, Z. anorg. Chem., 67, 234 (1910); 69, 215 (1911).
6. L. T. Jones, Ind. Eng. Chem., Anal. Ed., 14, 536 (1942).
7. R. N. Bell, Anal. Chem., 19, 97 (1947); 24, 1997 (1952).
8. O. T. Quimby and H. W. McCune, Anal. Chem., 29, 248 (1957).
9. C. B. Durgin, J. H. Lum, and J. E. Malowan, Trans. Am. Inst. Chem. Engrs., 33, 643 (1937).
10. R. N. Bell, Ind. Eng. Chem., 40, 1464 (1948).
11. E. Thilo and H. Grunze, Die papierchromatographie der kondensierten phosphaten, Akad. Verlag, Berlin, DDR, 1955.
12. E. Thilo and W. Feldmann, Z. anorg. Chem., 298, 316 (1959).
13. D. N. Bernhart and W. B. Chess, Anal. Chem., 31, 1026 (1959).
14. M. J. Smith, Anal. Chem., 31, 1023 (1959).
15. R. H. Kolloff, Anal. Chem., 33, 373 (1961).
16. A. L. Huhti and P. A. Gartaganis, Canad. J. Chem., 34, 785 (1956).
17. A. Simon and G. Schulze, Z. anorg. Chem., 242, 322 (1939).
18. A. Simon and M. Weist, Z. anorg. Chem., 268, 301 (1952).
19. P. J. Flory, J. Amer. Chem. Soc., 64, 2205 (1942).
20. J. R. Parks and J. R. van Wazer, J. Amer. Chem. Soc., 79, 4890–4897 (1957).
21. M. M. Striplin, Jnr., D. McKnight, and G. H. Megar, J. Agric. Food Chem., 6, 298 (1958).
22. Z. T. Wakefield and E. P. Egan, J. Agric. Food. Chem., 10, 344 (1962).
23. W. H. Ross and R. M. Jones, J. Amer. Chem. Soc., 47, 2166 (1925).
24. H. Bassett, J. Chem. Soc., 2949 (1958).
25. M. H. Giran, Compt. rend., 135, 961 (1902).
26. W. H. Ross and R. M. Jones, Ind. Eng. Chem., 17, 1170 (1925).
27. J. R. van Wazer, J. Amer. Chem. Soc., 72, 640 (1950).
28. Z. V. Kondratenko and I. G. Fedorchenko, Zhur. Neorg. Khim., 4, 985 (1959) [Russ. J. Inorg. Chem., No. 5 (1959)].
29. I. M. Mal'tseva, I. N. Shokin, and E. L. Yakhontova, Trudy Khim.-Tekhnol. Inst. im. Mendeleeva, No. 51, 225–229 (1966).
30. I. M. Mal'tseva, "Poluchenie i Issledovanie Svoistv Polifosfornoi Kisloty" (The Preparation and Study of the Properties of Polyphosphoric acid), Candidate's Thesis, Mendeleev Moscow Institute of Chemical Technology, 1966.
31. W. C. Scott, G. G. Paterson, and H. W. Elder, Ind. Eng. Chem., 53, 713 (1961).
32. A. Boulle and C. Morin, Compt. rend., 245, 1928 (1957).
33. D. C. Young and C. B. Scott, Chem. Eng. Progr., 59, No. 12, 80 (1963).
34. J. H. Walthall and M. M. Striplin, Ind. Eng. Chem., 33, 910 (1941).
35. M. M. Striplin, Ind. Eng. Chem., 33, 995 (1941).
36. D. McKnight and M. M. Striplin, Agric. Chem., 13, 833 (1958).
37. M. M. Striplin, Chem. Eng., 68, 19, 160–162 (1961).
38. Chem. Eng., 69, No. 20, 58 (1962).
39. N. N. Postnikov, M. G. Frenkel', B. I. Levi, P. F. Stepanov, and A. A. Brodskii, USSR P. 192 183 (1965); Byull. Izobr., No. 5, 33 (1967).
40. Tao-ho Huang, Ind. Eng. Chem., 53, 31 (1961).
41. I. Moldovan and M. Man, Rev. Chim. (RPR), 14, 437 (1963).
42. C. W. Davies and C. B. Monk, J. Chem. Soc., 413 (1949).
43. O. Samuelson, Svensk. kem. Tidskr., 61, 76 (1949).
44. R. Klement, Z. anorg. Chem., 260, 267 (1949).
45. J. R. van Wazer and K. A. Holst, J. Amer. Chem. Soc., 72, 640 (1950).
46. E. Thilo and K. H. Rattay, J. prakt. Chem., [4], 1, 14 (1954).
47. R. Klement and J. Schmid, Z. anorg. Chem., 290, 112 (1957).
48. T. Graham, Ann. Physik, 32, 33 (1834).
49. T. Fleitmann and W. Henneberg, Lieb. Ann., 65, 30, 387 (1845).
50. G. Tamman, J. prakt. Chem., 45, 417 (1892).
51. J. R. van Wazer and E. J. Griffith, J. Amer. Chem. Soc., 77, 6140 (1955).
52. J. R. van Wazer, C. F. Callis, and J. N. Shoolery, J. Amer. Chem. Soc., 77, 4945 (1955).
53. J. R. van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, J. Amer. Chem. Soc., 78, 5715 (1956).
54. C. F. Callis, J. R. van Wazer, J. N. Shoolery, and W. A. Anderson, J. Amer. Chem. Soc., 79, 2719–2726 (1957).
55. C. Romers, J. A. A. Ketelaar, and C. H. MacGillavry, Acta Cryst., 4, 114 (1951).
56. E. Thilo and H. Grunze, Z. anorg. Chem., 281, 263–283 (1955).
57. E. Kobayashi, J. Chem. Soc. Japan, Ind. Chem. Sect., 66, 583 (1963).
58. S. Ueda, J. Chem. Soc. Japan, Ind. Chem. Sect., 66, 591 (1963).

59. F. Kašparek, Acta univ. polack. olomuc., 9, 217 (1962).
60. S. I. Vol'fkovich and L. V. Kubasova, USSR P. 164 617 (5th July 1964).
61. E. Kobayashi, J. Chem. Soc. Japan, Ind. Chem. Sect., 72, 1474 (1969).
62. R. Klement and R. Poppo, Naturwiss., 44, 327 (1957).
63. E. Kobayashi, Rept. Govt. Chem. Ind. Res. Inst. Tokyo, 58, 397 (1963).
64. R. V. Coates and G. D. Woodard, J. Chem. Soc., 1780 (1964).
65. D. E. C. Corbridge and E. J. Lowe, J. Chem. Soc., 493 (1954).
66. A. W. Frazier, J. P. Smith, and J. R. Lehr, J. Agric. Food Chem., 13, 316 (1965).
67. T. D. Farr and J. D. Fleming, J. Chem. Data, 10, 20 (1965).
68. A. Norbert and M. J. Joucla, Compt. rend., 268, 243 (1969).
69. Y. Arai and S. Nagai, J. Chem. Soc. Japan, Ind. Chem. Sect., 69, 2077 (1969).
70. F. Kašpárek, Montash. Chem., 92, 1023 (1961); 93, 822 (1962).
71. T. D. Farr, J. D. Fleming, and J. D. Hatfield, J. Chem. Eng. Data, 12, 141 (1967).
72. E. Kobayashi, J. Chem. Soc. Japan, 85, 481 (1964).
73. H. Grunze and E. Thilo, Z. anorg. Chem., 281, 284 (1955).
74. C. Matignon and M. Dode, Bull. soc. chim. France, 5, 1114 (1934).
75. S. I. Vol'fkovich and A. I. Chekhovskikh, Zhur. Prikl. Khim., 39, 249 (1966).
76. A. I. Chekhovskikh, "Fosfaty Mocheviny" (Urea Phosphates), Candidate's Thesis, Chemistry Department, Moscow State University, 1966.
77. S. Ueda, K. Oyama, and K. Koma, J. Chem. Soc. Japan, Ind. Chem. Sect., 66, 586 (1963).
78. E. Kobayashi, J. Chem. Soc. Japan, Ind. Chem. Sect., 69, 2065 (1966).
79. E. Kobayashi, Rept. Gout. Chem. Ind. Res. Inst. Tokyo, 63, 263 (1968).
80. E. Steger, Z. anorg. Chem., 294, 146 (1958).
81. M. Shima, K. Namamoto, and S. Utsumi, Bull. Chem. Soc. Japan, 33, 1386 (1960).
82. O. R. Norchaeva, S. I. Vol'fkovich, L. V. Kubasova, and E. M. Popova, Zhur. Prikl. Khim., 43, 000 (1970).
83. J. G. Getsinger, J. Agric. Chem., 15, No. 10, 39 (1960).
84. J. G. Getsinger, M. R. Siegel, and H. C. Mann, J. Agric. Food Chem., 10, 341 (1962).
85. L. B. Nelson, Agric. Chem., 21, 20, 96 (1966).
86. L. V. Kubasova, Zhur. Prikl. Khim., 37, 955 (1964).
87. E. Kobayashi, J. Chem. Soc. Japan, Ind. Chem. Sect., 71, 807 (1968).
88. Chem. Process, 9, No. 3, 8–9 (1963).
89. T. P. Hignett and J. G. Getsinger, US P. 3 171 733 (2nd March 1965).
90. A. A. Ionass, T. Ya. Mysina, L. A. Bobkoca, and M. N. Kuznetsova, Trudy Nauch.-Issled. Inst. Udobrenii i Insektofungicidov, No. 1 (209), 141 (1968).
91. Chem. and Eng. News, 43, No. 39, 63 (1965).
92. E. V. Britske and A. P. Dunaev, Zhur. Prikl. Khim., 2, 162 (1928).
93. L. Harris and C. B. Wooster, J. Amer. Chem. Soc., 51, 2121 (1929).
94. A. Sanfourche, A. Hernette, and M. Fau, Bull. Soc. Chim. France, 47, 273 (1930).
95. S. I. Vol'fkovich, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 767 (1957).
96. M. Becke-Goehring and J. Sambeth, Z. anorg. Chem., 297, 287 (1958).
97. J. M. Stinson, M. M. Striplin, Jnr., N. A. Brown, and L. F. Seatz, J. Agric. Food Chem., 4, 248 (1956).
98. P. S. Bozadzhiev, S. I. Vol'fkovich, and A. I. Chekhovskikh, Zhur. Prikl. Khim., 40, 895 (1967).
99. S. I. Vol'fkovich and T. I. Sokolova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 661 (1957).
100. Japanese P. 15 603 (14th March 1960); Ref. Zhur. Khim., 4 (1966).
101. E. Kobayashi, J. Chem. Soc. Japan, Ind. Chem. Sect., 64, 117, 955 (1961).
102. E. Kobayashi, Rept. Gov. Chem. Indust. Res. Inst. (Tokyo), 58, 315 (1963).
103. E. Kobayashi, J. Chem. Soc. Japan, 83, 136 (1962).
104. A. V. Slack, J. M. Potts, and H. B. Shaffer, J. Agric. Food Chem., 13, 165 (1965).
105. D. C. Young, US P. 3 044 851 (17th July 1962).
106. J. A. Wilbanks, M. C. Nason, and W. C. Scott, J. Agric. Food Chem., 9, 174 (1961).
107. Commercial Fert. and Plant Food Industry, 97, No. 2, 28 (1958).
108. Oil, Paint, and Drug Report, 182, No. 2, 4 (1963).
109. L. V. Kubasova, "Degidratirovannye Fosfaty Ammoniya" (Dehydrated Ammonium Phosphates), Candidate's Thesis, Chemistry Department, Moscow, State University, 1964.
110. L. V. Kubasova, in collected papers, "Issledovaniya po Khimii i Tekhnologii Udobrenii, Pestitsidov, Solei" (Collected Papers on the Chemistry and Technology of Fertilisers, Pesticides, and Salts), Izd. Nauka, Moscow, 1966, p. 151.
111. J. R. van Wazer, J. Amer. Chem. Soc., 72, 644 (1950).
112. S. I. Vol'fkovich, M. V. Lykov, and A. S. Cherepanova, Zhur. Prikl. Khim., 39, 3 (1966).
113. R. G. Aziev, "Fiziko-khimicheskoe Issledovanie Termicheskoi Dissotsiatsii Fosfatov Kal'tsiya" (A Physicochemical Study of the Thermal Dissociation of Calcium Phosphates), Candidate's Thesis, Chemistry Department, Moscow State University, 1967.

Department of Chemical
Technology, Lomonosov
Moscow State University