

50% greater than in mixture G. The sulfate concentration was varied in the same manner as with mixture G. Weight loss was greater in mixture H than in mixture G, but dropped sharply as the sulfate concentration increased and approached a minimum of 5.0 grams as the mole ratio approached 1 to 1.

Mixture I, which contained 50% less ammonium nitrate than mixture G, did not lose so much weight as mixture G, as was expected. The losses again reached a minimum at about the same mole ratio of sulfate ion to monocalcium phosphate as in mixture G and H. For comparison of the results of the runs made with the G, H, and I series of samples, the weight loss data for all runs were plotted against the $\text{SO}_4^{-2}/\text{Ca}(\text{H}_2\text{PO}_4)_2$ mole ratio in Figure 6 and the $\text{SO}_4^{-2}/\text{NH}_4\text{NO}_3$ mole ratio in Figure 7. Maximum stability is obtained in all three mixtures as the $\text{SO}_4^{-2}/\text{Ca}(\text{H}_2\text{PO}_4)_2$ mole ratio reaches 1 to 1. This is not true as the $\text{SO}_4^{-2}/\text{NH}_4\text{NO}_3$ mole ratio approaches 1 to 1 in the fertilizer mixtures. In mixture H, maximum stability is reached at a $\text{SO}_4^{-2}/\text{NH}_4\text{NO}_3$ mole ratio of 0.5 to 1, and in mixture I, at a 2 to 1 mole ratio.

These results indicate that an important factor in inhibiting the decomposition is to prevent the formation of free acid in the mixture. This can be accomplished by adding either ammonium sulfate or potassium sulfate to the fertilizer.

Conclusions

The stability of laboratory fertilizer mixtures was found to be dependent upon temperature, acidity, concentration of chloride and sulfates, and the presence of both ammonium and nitrate ions. Under certain conditions decomposition of the samples was initiated at temperatures as low as 100° C. and the rate of decomposition increased rapidly with temperature. Nitrogen, nitrous oxide, and chlorine were identified as the principal gaseous reaction products.

A key reaction in decomposition was the hydrolysis of monocalcium phosphate, which resulted in the formation of dicalcium phosphate and phosphoric acid. Reaction of the acid, ammonium nitrate, and ammonium chloride caused substantial losses of nitrogen and chloride

from the fertilizer mixtures. The effects obtained in these tests are those which would be observed during the commercial manufacture of fertilizer blends where unammoniated superphosphate is used. The stabilizing effect of ammonium sulfate or potassium sulfate in the fertilizer blends was conclusively demonstrated.

Literature Cited

- (1) Besson, M., Rosset, M., *Compt. Rend.* **142**, 633-4 (1906).
- (2) Borland, C. C., Schall, E. D., *J. Assoc. Offic. Agr. Chemists* **42**, 579-86 (1959).
- (3) Rozman, B. Y., *J. Appl. Chem. USSR* **33**, 1052-9 (1960).
- (4) Saunders, H. L., *J. Chem. Soc. (London)* **121**, 698-711 (1922).
- (5) Shah, M. S., Oza, T. M., *Ibid.*, **131**, 726-36 (1932).
- (6) Tennessee Valley Authority, *Farm Chem.* **122**, 24-8 (July 1959).
- (7) Tramm, H., Velde, H., *Angew. Chem.* **47**, 782-3 (1934).

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FERTILIZER MATERIALS

Characterization of Some Ammonium Polyphosphates

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Methods of preparation and crystallographic properties are described for six ammonium pyrophosphates, six ammonium tripolyphosphates, an ammonium nitrate pyrophosphate, and a long-chain ammonium polyphosphate. The information will be useful in identification of these compounds in ammonium polyphosphate fertilizers.

AMMONIUM polyphosphate fertilizers, products of the reaction of ammonia with superphosphoric acid (10), are mixtures of the ammonium salts of ortho-, pyro-, and more highly condensed phosphoric acids. As these materials are finding increasing use as fertilizers, the properties of their individual components are being studied. Fourteen of these components are described here—six pyrophosphates, six tripolyphosphates, a long-chain polyphosphate, and an ammonium nitrate pyrophosphate.

The sodium and potassium salts of condensed phosphoric acids have been studied extensively (12), but the ammonium salts have been neglected because they have been thought to be unstable and difficult to prepare as pure compounds. Studies of the solubilities of the ammonium pyro- (5) and tri-

polyphosphates, however, showed these salts to be easily prepared and moderately stable.

Ammonium salts of condensed phosphoric acids are reported in the literature (3, 4, 7, 8, 11, 12), but their crystallographic descriptions are incomplete, and some of the reported compositions are in error.

Preparation and Characterization

All the salts were either prepared from recrystallized reagents or obtained as solid phases in solubility determinations (5). Characterizations were made only on preparations that were shown by petrographic examination to be homogeneous and well crystallized, gave consistent x-ray powder diffraction spectra, and had the same chemical composition from preparation to preparation.

Chemical analyses were made on air-

dried preparations to prevent dehydration or other alteration which might occur above room temperature. The hydrate water contents of some of the preparations, which were determined by difference, are slightly high. All the preparations were examined by paper chromatography to verify the phosphate species. Phosphorus was determined photometrically (6) and ammonia was determined by distillation with sodium hydroxide.

Morphological and optical properties were determined with a polarizing microscope. Densities of all the salts were calculated from their chemical compositions and refractive indices by the Gladstone-Dale relationship (9); densities of coarsely crystalline materials were determined also from single-crystal x-ray data.

X-ray diffraction spectra were obtained with a Norelco high-angle goniometer and $\text{CuK}\alpha$ radiation ($\lambda = 1.5405$ A.). Lattice constants and space-group

symmetry were determined by equi-inclination Weissenberg camera techniques.

Three sources of condensed phosphates were used. Passage of solutions of $\text{Na}_4\text{P}_2\text{O}_7$ or $\text{Na}_5\text{P}_3\text{O}_{10}$ through acid-treated Amberlite IR-120 resin yielded solutions of the corresponding acids which were ammoniated immediately and evaporated under vacuum (5). To prevent hydrolysis of the condensed phosphate, all these operations were carried out below 10°C .

Ammonium triphosphates were prepared by fractional crystallization from products of the ammoniation of electric-furnace superphosphoric acid that contained 35 to 36% P (79 to 82% P_2O_5). The crude $(\text{NH}_4)_3\text{P}_3\text{O}_{10}\cdot\text{H}_2\text{O}$ was purified by eight recrystallizations; the other triphosphates were prepared by lowering the pH of solutions of this salt with Amberlite IR-120 resin and treating the eluate with ethanol. The desired salt frequently separated as an oil that crystallized on seeding or agitation.

Ammonium pyrophosphates were prepared by treating aqueous solutions or suspensions of calcium ammonium pyrophosphates (7, 2) with ammonium fluoride. The precipitated calcium fluoride was separated, and ethanol was added to the filtrates to precipitate the ammonium pyrophosphates, which were then recrystallized from water. Addition of calcium carbonate to an aqueous solution of ammoniated superphosphoric acid precipitated $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7\cdot\text{H}_2\text{O}$; treatment of an aqueous suspension of this salt with ammonium fluoride yielded a solution of ammonium

Table I. Composition of Ammonium Polyphosphates

Compound	Composition, %					Moles/Mole P	
	N	P	NH_3	P_2O_5	H_2O (diff.)	N	Hydrate H_2O
$(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$							
Orthorhombic	12.8	28.3	15.5	64.8	11.5	1.00	0.20
Monoclinic	13.0	28.9	15.8	66.3	9.5	1.00	0.07
Stoichiometric	13.21	29.24	16.04	66.98	8.49	1.00	0.00
$(\text{NH}_4)_3\text{HP}_2\text{O}_7$							
Stoichiometric	18.1	26.8	22.0	61.5	4.9	1.50	0.06
	18.34	27.07	22.27	62.01	3.93	1.50	0.00
$(\text{NH}_4)_3\text{HP}_2\text{O}_7\cdot\text{H}_2\text{O}$							
Stoichiometric	16.8	25.0	20.5	57.4	11.3	1.50	0.53
	17.00	25.10	20.65	57.49	10.93	1.50	0.50
$(\text{NH}_4)_4\text{P}_2\text{O}_7$							
Stoichiometric	21.9	25.0	26.6	57.3	2.0	1.94	0.15
	22.77	25.20	27.64	57.72	0.00	2.00	0.00
$(\text{NH}_4)_3\text{P}_3\text{O}_7\cdot\text{H}_2\text{O}$							
Stoichiometric	20.7	23.6	25.2	54.0	7.5	1.95	0.55
	21.21	23.49	25.75	53.79	6.82	2.00	0.50
$\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_3\text{HP}_2\text{O}_7\cdot\text{H}_2\text{O}$							
Stoichiometric	17.7 ^a	19.3	21.5	44.2	7.9	2.04 ^a	0.51
	17.12 ^b	18.96	20.79	43.43	8.27	2.00 ^b	0.50
$(\text{NH}_4)_3\text{H}_2\text{P}_3\text{O}_{10}$							
Stoichiometric	13.4	29.9	16.2	68.5	6.7	1.00	0.07
	13.59	30.49	16.50	68.93	5.83	1.00	0.00
$(\text{NH}_4)_3\text{H}_2\text{P}_3\text{O}_{10}\cdot\text{H}_2\text{O}$							
Stoichiometric	12.9	28.2	15.7	64.7	11.3	1.00	0.34
	12.84	28.44	15.59	65.14	11.01	1.00	0.33
$(\text{NH}_4)_3\text{HP}_3\text{O}_{10}$							
Stoichiometric	16.3	28.5	19.8	65.4	4.4	1.27	0.10
	17.18	28.53	20.86	65.34	2.76	1.33	0.00
$(\text{NH}_4)_3\text{H}(\text{P}_3\text{O}_{10})_2\cdot 2\text{H}_2\text{O}$							
Stoichiometric	17.6	26.2	21.4	60.1	7.2	1.49	0.37
	17.87	26.38	21.70	60.43	6.38	1.50	0.33
$(\text{NH}_4)_3\text{P}_3\text{O}_{10}\cdot\text{H}_2\text{O}$							
Stoichiometric	19.3	25.6	23.4	58.7	5.5	1.67	0.37
	19.39	25.76	23.54	59.00	4.99	1.67	0.33
$(\text{NH}_4)_3\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$							
Stoichiometric	18.5	24.5	22.5	56.2	9.4	1.67	0.66
	18.47	24.54	22.43	56.20	9.50	1.67	0.67
$(\text{NH}_4)_{n+2}\text{P}_n\text{O}_{3n+1}^c$							
Stoichiometric ^d	14.3	31.8	17.4	72.9	0.4	1.00	...
	14.85	31.62	18.03	72.42	0.00	1.04	...

^a $\text{NH}_3\text{-N}$; contains also 3.9% $\text{NO}_3\text{-N}$, 0.45 mole NO_3 /mole P.

^b $\text{NH}_3\text{-N}$; contains also 4.28% $\text{NO}_3\text{-N}$, 0.50 mole NO_3 /mole P.

^c Corrected to dry basis after determination of free water.

^d When $n = 5$. Within precision of analytical data, $n = 51 \pm 8$.

Table II. Morphological and Optical Properties of Ammonium Pyrophosphates

Compound	Crystal System, Class, and Habit	Refractive Indices	Optical Properties ^a
$(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7^b$	Monoclinic, $2/m$. Tabular on (100), elongated along c ; modifying forms {011}, {010}, and {120}	$\alpha = 1.505$ $\beta = 1.521$ $\gamma = 1.556$	Biaxial (+), $2V = 65\text{--}70^\circ$ (69°). OAP = (010), with $N_\gamma \wedge c$ on (010) = 4° in acute β ; $\beta = 108.5^\circ$, $d = 1.89$
$(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7^c$	Orthorhombic, mmm . Thin rectangular plates contg. N_β and N_γ , elongated along N_γ	$\alpha = 1.495$ $\beta = 1.505$ $\gamma = 1.521$	Biaxial (+), $2V = (77^\circ)$. N_α and OAP \perp to tabular plane, $d = 1.81$
$(\text{NH}_4)_3\text{HP}_2\text{O}_7$	Monoclinic, $2/m$. Tabular on (010), elongated along a ; modifying forms {021}, {120}, and {121}	$\alpha = 1.518$ $\beta = 1.521$ $\gamma = 1.531$	Biaxial (+), $2V = 55^\circ$ (57°). OAP \perp (010) with $N_\gamma = b$; $N_\beta \wedge c = 37^\circ$ in acute β . Monoclinic $\beta = 110.8^\circ$. Dispersion, $r > v$, is weak. $d = 1.73$
$(\text{NH}_4)_3\text{HP}_2\text{O}_7\cdot\text{H}_2\text{O}$	Triclinic, $\bar{1}$. Rods flattened on (100) and elongated along b ; b -zone forms are {101}, {001}, and {100}; terminal forms are (111), ($\bar{1}\bar{1}\bar{1}$), {010}, and the pair (110) and ($\bar{1}\bar{1}\bar{0}$)	$\alpha = 1.494$ $\beta = 1.509$ $\gamma = 1.517$	Biaxial (-), $2V = 65\text{--}70^\circ$ (71°). The OAP and N_γ nearly \perp to (001), with OAP inclined about 52° to b on (001) in acute γ . Dispersion, $r > v$, is weak. $d = 1.66$
$(\text{NH}_4)_4\text{P}_2\text{O}_7$	Monoclinic, $2/m$. (001) tablets, with elongation along a ; forms {001}, {101}, {100}, and prominent {111}	$\alpha = 1.514$ $\beta = 1.520$ $\gamma = 1.521$	Biaxial (-), $2V = 45^\circ$ (44°). OAP \perp to (010), with $b = N_\gamma$. $N_\alpha \wedge a$ on (010) = 16° in acute β ; $\beta = 105^\circ$. No dispersion. $d = 1.61$
$(\text{NH}_4)_4\text{P}_2\text{O}_7\cdot\text{H}_2\text{O}$	Monoclinic, $2/m$. Rods elongated on c , with prominent {110}, and {001}, {011}, {101}, sometimes {010}. Cyclic twinning on (110) very common	$\alpha = 1.496$ $\beta = 1.498$ $\gamma = 1.503$	Biaxial (+), $2V = 65\text{--}70^\circ$ (65°). OAP \perp to (010); $N_\alpha = b$; $N_\gamma \wedge c$ on (010) = 25° in obtuse β ; $\beta = 104^\circ$. $d = 1.54$
$\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_3\text{HP}_2\text{O}_7\cdot\text{H}_2\text{O}$	Triclinic, $\bar{1}$. Plates tabular on (100) and elongated along c . Forms {010}, {101}, {011}, sometimes {001}; $\alpha = 118^\circ$, $\beta = 110^\circ$, and $\gamma = 61^\circ$	$\alpha = 1.461$ $\beta = 1.506$ $\gamma = 1.523$	Biaxial (-), $2V = 60^\circ$ (61.5°). OAP nearly \perp to (100) and \parallel to c , with N_α nearly \perp to (100) also. $d = 1.60$

^a Calculated values for $2V$ in parentheses. All values for densities calculated.

^b Dimorphic form stable at room temperature; γ form (3).

^c Dimorphic form stable above room temperature; α form (3).

Table IV. Morphological and Optical Properties of Ammonium Tripolyphosphates

Compound	Crystal System, Class, and Habit	Refractive Indices	Optical Properties ^a
(NH ₄) ₃ H ₂ P ₃ O ₁₀	Monoclinic, 2/m. Tabular on (100), and elongated along <i>a</i> ; modifying forms are {011}, {010}, and partial set (111), (111), (111), (111)	$\alpha = 1.475$ $\beta = 1.487$ $\gamma = 1.509$	Biaxial (+), 2 <i>V</i> ~75° (79°). OAP = (010), with <i>N</i> _γ ∧ <i>c</i> = 26° in obtuse β. β = 126°, <i>d</i> . = 1.76
(NH ₄) ₃ H ₂ P ₃ O ₁₀ ·H ₂ O	Monoclinic, 2/m. Prisms elongated along <i>a</i> , showing prominent set {011}, and {111} as terminal forms; habits are pseudo-orthorhombic in appearance	$\alpha = 1.471$ $\gamma = 1.483$ $\gamma = 1.488$	Biaxial (-), 2 <i>V</i> = 60° (65°). OAP ⊥ to (010), and virtually to (001); <i>N</i> _β = <i>b</i> , <i>N</i> _α = <i>a</i> ; nearly symmetrical extinction contributes to pseudoorthorhombic appearance. <i>d</i> . = 1.71
(NH ₄) ₄ HP ₃ O ₁₀	Monoclinic, 2/m. (100) plates, elongated along <i>b</i> , beveled by {101} and {001}, and terminated by partial set (111), (111), (111), and (111)	$\alpha = 1.488$ $\beta = 1.509$ $\gamma = 1.511$	Biaxial (-), 2 <i>V</i> = 30° (34°). OAP = (010), with <i>N</i> _γ ∧ <i>a</i> = 26° in obtuse β; β = 109° (<i>B</i> _{xa} slightly tilted to <i>a</i>). <i>d</i> . = 1.72
(NH ₄) ₃ H(P ₃ O ₁₀) ₂ ·2H ₂ O	Monoclinic, 2/m. Tabular on (001), and elongated along <i>b</i> , with modifying forms {100} and {211}; [often incomplete as (211), (211), (211), and (211)]	$\alpha = 1.508$ $\beta = 1.512$ $\gamma = 1.515$	Biaxial (-), 2 <i>V</i> near 90° (82°). OAP = (010), with <i>N</i> _γ ∧ <i>a</i> = 40° in obtuse β; β = 112°; <i>N</i> _β = <i>b</i> . One optic axis nearly ⊥ to (001). <i>d</i> . = 1.69
(NH ₄) ₃ P ₃ O ₁₀ ·H ₂ O	Triclinic, 1. (010) plates elongated along <i>c</i> , modified by the equally developed forms {120}, {021}, and {101}. Pronounced pseudoorthorhombic symmetry; α, β, and γ each about 90°	$\alpha = 1.501$ $\beta = 1.505$ $\gamma = 1.512$	Biaxial (+), 2 <i>V</i> = 70° (74°). OAP and <i>N</i> _α nearly ⊥ to (010), with <i>N</i> _β nearly to <i>c</i> (elong. axis). <i>N</i> _β ∧ <i>c</i> = 6-7° in obtuse β. <i>d</i> . = 1.63
(NH ₄) ₃ P ₃ O ₁₀ ·2H ₂ O	Monoclinic, 2/m. Tabular on (001), and elongated along <i>b</i> ; modifying forms are {110} and {100}. β = 100°	$\alpha = 1.500$ $\beta = 1.505$ $\gamma = 1.507$	Biaxial (-), 2 <i>V</i> = 65° (64°). OAP ⊥ to (010), with <i>N</i> _β ∧ <i>c</i> = 12° in obtuse β. <i>N</i> _α nearly coincides with <i>a</i> in tabular plane. <i>N</i> _γ = <i>b</i> . <i>d</i> . = 1.62

^a Calculated values for 2*V* in parentheses. All values for densities calculated.

Table V. Lattice Constants of Ammonium Pyro- and Tripolyphosphates

Unit-Cell Contents	Crystal System	Probable Space Group	Lattice Constants				Density	
			<i>a</i> ₀	<i>b</i> ₀	<i>c</i> ₀	β	X-ray	Optical ^a
4[(NH ₄) ₃ H ₂ P ₂ O ₇]	Monoclinic	<i>C</i> ₂ ^s <i>h</i> - <i>P</i> 2 ₁ / <i>c</i>	7.36	11.26	9.06	108.5°	1.86	1.89
4[(NH ₄) ₃ HP ₂ O ₇]	Monoclinic	<i>C</i> ₂ ^s <i>h</i> - <i>P</i> 2 ₁ / <i>c</i>	6.63	19.74	7.09	111.0°	1.75	1.73
2[(NH ₄) ₃ HP ₂ O ₇ ·H ₂ O]	Triclinic ^b	<i>C</i> ₁ ¹ - <i>P</i> 1	9.13	6.33	9.96	77.2°	1.67	1.66
4[(NH ₄) ₃ P ₂ O ₇]	Monoclinic	<i>C</i> ₂ ^s <i>h</i> - <i>C</i> 2/ <i>c</i>	11.77	6.51	13.63	104.7°	1.61	1.61
2[(NH ₄) ₃ H ₂ P ₃ O ₁₀]	Monoclinic	<i>C</i> ₂ ^s <i>h</i> - <i>P</i> 2/ <i>c</i>	7.59	10.90	8.78	126.1°	1.74	1.76
4[(NH ₄) ₃ H ₂ P ₃ O ₁₀ ·H ₂ O]	Monoclinic	<i>C</i> ₂ ^s <i>h</i> - <i>P</i> 2 ₁ / <i>c</i>	7.31	8.08	21.73	101.2°	1.71	1.71
4[(NH ₄) ₃ HP ₃ O ₁₀]	Monoclinic	<i>C</i> ₂ ^s <i>h</i> - <i>C</i> 2/ <i>c</i>	14.24	7.47	12.59	109.5°	1.71	1.72
4[(NH ₄) ₃ H(P ₃ O ₁₀) ₂ ·2H ₂ O]	Monoclinic	<i>C</i> ₂ ^s <i>h</i> - <i>C</i> 2/ <i>c</i>	22.71	6.98	18.86	112.2°	1.69	1.69
6[(NH ₄) ₃ P ₃ O ₁₀ ·H ₂ O]	Triclinic ^c	<i>C</i> ₁ ¹ - <i>P</i> 1	10.94	31.5	6.43	90 ± 0.2°	1.61	1.63

^a Calculated by Gladstone-Dale relationship from refractive indices (8).

^b α = 115.4°, γ = 109.2°.

^c Angles α and γ (like angle β) are essentially 90°, in accord with pronounced pseudoorthorhombic symmetry observed for well crystallized preparations.

in Table I; their crystallographic properties are shown in Table IV, and their x-ray diffraction patterns are listed in Table III.

Triammonium Tripolyphosphate. Coarse crystals of anhydrous (NH₄)₃H₂P₃O₁₀ were prepared by adding Amberlite IR-120 resin to a 10% aqueous solution of tetra- or pentaammonium tripolyphosphate to lower the pH below 3, decanting off the liquid phase and precipitating with ethanol a tripolyphosphate oil that crystallized in about 12 hours. The crystallization could be accelerated by seeding and stirring, but the product then consisted of aggregates of smaller crystals that often contained uncrystallized oil and were difficult to dry completely.

At room temperature (NH₄)₃H₂P₃O₁₀ is stable and nonhygroscopic.

Triammonium Tripolyphosphate Monohydrate. The hydrate (NH₄)₃H₂P₃O₁₀·H₂O was prepared in the same way as the anhydrous salt, except crystallization was carried out below 10° C.

At room temperature, (NH₄)₃H₂P₃O₁₀·H₂O slowly dehydrates to the anhydrous salt on exposure to the laboratory atmosphere.

Tetrammonium Tripolyphosphate. Evaporation of a solution of ammonium tripolyphosphate (pH 4) yielded crystals of (NH₄)₄HP₃O₁₀; treatment of the solution with ethanol frequently yielded an oil which crystallized slowly. The salt is stable and nonhygroscopic at room temperature.

Nonaammonium Tripolyphosphate Dihydrate. The pH of a moderately concentrated solution of pentaammonium tripolyphosphate was adjusted to 5 with Amberlite resin or acetic acid, and ethanol was added. The oil that separated crystallized readily as (NH₄)₉H(P₃O₁₀)₂·2H₂O. This salt precipitates from solution in a narrow range of pH and is frequently obtained as a contaminant in preparations of tetra- and pentaammonium tripolyphosphates. The crystals are nonhygroscopic and stable at room temperature.

Pentaammonium Tripolyphosphate Monohydrate. The pH of a concentrated solution of ammonium tripolyphosphate was adjusted to 6; on treatment of the solution at 25° to 50° C. with ethanol an oil separated that crystallized rapidly as characteristic plates of (NH₄)₅P₃O₁₀·H₂O. The monohydrate is obtained also from the spontaneous dehydration of the dihydrate at room temperature.

The monohydrate is stable and nonhygroscopic at room temperature. On heating, decomposition begins at 55° C. and is rapid at 100° C. The products of the decomposition are tri- and tetraammonium pyrophosphates, but no orthophosphates.

Pentaammonium Tripolyphosphate Dihydrate. Electric-furnace superphosphoric acid (35% P, 80% P₂O₅) was ammoniated to pH 6 or above and the solution was cooled below 10° C., whereupon blade crystals of crude (NH₄)₅P₃O₁₀·2H₂O formed. The dihydrate was purified by several crys-

tallizations from water at the temperature of 0° C.

The dihydrate is stable in pure solutions at 0° to 10° C., and it appeared at higher temperatures as a metastable phase in solutions containing pyro- and orthophosphates. In pure solutions above 10° C., only the monohydrate crystallized.

On exposure to the atmosphere at room temperature, $(\text{NH}_4)_3\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ rapidly dehydrates to the monohydrate. When precipitated rapidly, the dihydrate forms felted crystal masses that are difficult to dewater without some dehydration to the monohydrate.

Long-Chain Ammonium Polyphosphate. A finely divided crystalline long-chain ammonium polyphosphate appeared when the product of ammoniation of superphosphoric acid containing 36 to 37% P (83 to 84% P_2O_5) was placed in water, although this salt was not present in the initial product. The salt crystallized rapidly as dissolution of the clear ammonium polyphosphate gel proceeded, and contained 35 to 40% of the P in the original material, or virtually all the highly condensed polyphosphate originally present. The salt was filtered off, washed with water and then with acetone, and air-dried. Its composition, Table I, was that of $(\text{NH}_4)_{n+2}\text{P}_n\text{O}_{3n-1}$ in which n is 50 or more.

The dry crystals are stable at room temperature, even at high humidity. The salt remained unchanged crystallographically on heating at 105° C. for 48 hours. Its rate of solution was very low—only 0.1 gram dissolved in 100 ml. in 24 hours at 25° C. Differential thermal analysis (heating rate, 10° C. per minute) showed only one peak, endothermic, where the salt melted at 355° C.

Discussion

The formula assigned to each salt is based on the composition (Table I) of at least three homogeneous crystalline preparations. Single-crystal x-ray studies were made of all the reasonably stable salts that were obtained as large enough crystals; their lattice constants are shown in Table V.

Although the literature contains numerous references to condensed ammonium phosphates, the descriptions usually refer to mixtures rather than individual salts. Ammonium pyrophosphates are reported as products of thermal treatment of mono- (7) and diammonium orthophosphates (8); thermal treatment of triammonium orthophosphate is reported to yield di- and triammonium pyrophosphate (7). Tetrammonium pyrophosphate has been prepared (12), but only its infrared absorption spectrum (4) and its x-ray diffraction spectrum (ASTM 11-634) are reported; results of this study show

that the reported spectra are those of anhydrous $(\text{NH}_4)_4\text{P}_2\text{O}_7$ rather than the monohydrate. An infrared spectrum is reported also for the compound $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ (4), but no hydrate of diammonium pyrophosphate was observed in this study; the x-ray pattern (ASTM 11-632) is that of the monoclinic dimorph of $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$. In general, the x-ray spectra obtained in the present study are in good agreement with those of the ammonium pyro- and triphosphates reported by Coates and Woodward (3).

Kobayashi (8) reported the preparation of $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$, $(\text{NH}_4)_3\text{HP}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$, and $(\text{NH}_4)_4\text{P}_2\text{O}_7 \cdot 4.5\text{H}_2\text{O}$ and gave their partial x-ray diffraction patterns. His pattern for $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$ is similar to that of the monoclinic dimorph but includes lines that do not appear in the patterns of either dimorph of this salt. Neither the composition nor the x-ray diffraction pattern he reported for $(\text{NH}_4)_3\text{HP}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ was confirmed in this study. The x-ray diffraction pattern ascribed to $(\text{NH}_4)_4\text{P}_2\text{O}_7 \cdot 4.5\text{H}_2\text{O}$ agrees closely, except for two lines, with that of $(\text{NH}_4)_4\text{P}_2\text{O}_7$.

The only published information on the ammonium tripolyphosphates is an x-ray diffraction pattern (ASTM 11-633) for a salt with the reported composition $(\text{NH}_4)_5\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$.

Stability of Ammonium Pyrophosphates. In closed containers at room temperature, most of the ammonium pyrophosphates remained unchanged. In the open, however, there were slow loss of ammonia and alteration from tetra- to tri- to diammonium pyrophosphate and also loss of hydrate water. Loss of ammonia by tetraammonium pyrophosphate was accelerated by moisture and was rapid at relative humidities of 50% or more, but triammonium pyrophosphate lost ammonia slowly at all humidities to form the monoclinic diammonium pyrophosphate.

Tetraammonium pyrophosphate monohydrate dehydrates readily, and preparations of this hydrate must be stored immediately in closed containers to avoid contamination with the anhydrous salt. The anhydrous salt hydrates to the monohydrate at relative humidities above 50%.

Losses of ammonia and hydrate water are accelerated by rise in temperature and become rapid at about 55° C. On rapid heating, the ammonium pyrophosphates soften or melt with decomposition in the range 100° to 115° C. Both tetra- and triammonium pyrophosphates yielded mixtures of $\text{NH}_4\text{H}_2\text{PO}_4$ and orthorhombic $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$. Prolonged heating of either dimorph of diammonium pyrophosphate yielded $\text{NH}_4\text{H}_2\text{PO}_4$ and an amorphous phase. Orthorhombic diammonium pyrophosphate appears to be the high-temperature dimorph, in accord with its

higher symmetry and lower density; at room temperature it alters slowly to the monoclinic dimorph.

Products of the ammoniation of superphosphoric acid (32 to 35% P, 75 to 82% P_2O_5) consist mainly of ammonium ortho- and pyrophosphates. At low degrees of ammoniation (mole ratio N:P = 1.1 to 1.2), the products are mostly mixtures of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_3\text{HP}_2\text{O}_7$; at higher degrees of ammoniation (mole ratio N:P = 1.9 to 2.0), the products are mostly $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$ and $(\text{NH}_4)_4\text{P}_2\text{O}_7$. The pyrophosphates in these mixtures behave the same as they do alone, and the alterations due to loss of ammonia and change in hydration, which are influenced by temperature and humidity, determine the behavior of the products in storage.

Stability of Ammonium Tripolyphosphates. Only a brief study was made of the stability of the ammonium tripolyphosphates. On heating, $(\text{NH}_4)_5\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ decomposes rapidly at 95° to 105° C. to $(\text{NH}_4)_4\text{P}_2\text{O}_7$ and then to $(\text{NH}_4)_3\text{HP}_2\text{O}_7$; no significant amounts of orthophosphate are formed. The final product was more than 90% pyrophosphate—the rest was tripolyphosphate and a trace of orthophosphate. It is concluded either that thermal hydrolysis of dissolved or molten tripolyphosphate proceeds only to pyrophosphate or that any orthophosphate formed is rapidly condensed to pyrophosphate.

Significant amounts of ammonium tripolyphosphates formed only from superphosphoric acids that contained at least 36% P (83% P_2O_5). When liquid fertilizers prepared from these highly concentrated acids are stored at temperatures near 0° C., relatively large amounts of $(\text{NH}_4)_5\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ precipitate. When separated and dried, these crystals dehydrate rapidly to the monohydrate.

Ammonium Nitrate Pyrophosphate. On storage for a year in closed containers, $\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ remained unchanged.

Another ammonium nitrate pyrophosphate has been prepared, but only in amounts inadequate for characterization; its composition is thought to be $\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$. It was obtained as a single-phase product only once, when it crystallized slowly from a chilled, highly acidic (pH less than 2), concentrated solution of an equimolar mixture of NH_4NO_3 and $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$; its preparations usually are contaminated with other pyrophosphates. This mixed salt can sometimes be crystallized from seeded, slowly cooled melts of an equimolar mixture of NH_4NO_3 and $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$. Its crystals have hexagonal-hemimorphic symmetry, with prominent basal (001) forms modified by a set of pyramidal forms (zincite type); birefringence is extreme, $N_e = 1.375$,

$N_w = 1.476$; the crystals are uniaxial (—).

Long-Chain Ammonium Polyphosphate. The preparations of the long-chain ammonium polyphosphate showed consistent optical properties, x-ray diffraction pattern, and chemical composition—that of $(\text{NH}_4)_{n+2}\text{P}_n\text{O}_{3n+1}$, approaching $(\text{NH}_4\text{FO}_3)_x$. It crystallized as microscopic stubby rods that were rectangular prismatic and showed parallel extinction; $N_\alpha = 1.485$ (elongation axis), $N_\gamma = 1.500$. The symmetry appears to be orthorhombic or higher, in accordance with its relatively simple x-ray diffraction pattern. Crystals large enough for detailed optical examination or for single-crystal x-ray study have not been prepared, but study of the material is being continued.

This ammonium polyphosphate

showed no close similarity to Maddrell's or Kurrol's salts in optical properties or x-ray diffraction pattern; the features of its infrared absorption spectrum were similar to those of the form IV Kurrol salts and unlike those of the cyclic alkali metal metaphosphates. The infrared spectrum contained no evidence of the presence of any -P-N-P- linkages. The salt has the desirable fertilizer property of being a slowly soluble, single source of both nitrogen and phosphorus.

Literature Cited

- (1) Brown, E. H., Lehr, J. R., Frazier, A. W., Smith, J. P., *J. Agr. Food Chem.* **12**, 70 (1964).
- (2) Brown, E. H., Lehr, J. R., Smith, J. P., Frazier, A. W., *Ibid.*, **11**, 214 (1963).

- (3) Coates, R. V., Woodward, G. D., *J. Chem. Soc.* **1964**, p. 1780.
- (4) Corbridge, D. E. C., Lowe, E. J., *Ibid.*, **1954**, p. 493.
- (5) Farr, T. D., Fleming, J. D., *J. Chem. Eng. Data* **10**, 20 (1965).
- (6) Gee, A., Deitz, V. R., *Anal. Chem.* **25**, 1320 (1953).
- (7) Kasperek, F., *Acta Univ. Palackianae Olomuc., Fac. Rerum Nat.* **9**, 217 (1962).
- (8) Kobayashi, E., *Nippon Kagaku Zasshi* **83**, 132 (1962).
- (9) Larsen, E. S., Berman, H., U. S. Geol. Survey, Bull. **848** (1934).
- (10) Striplin, M. M., Jr., *Chem. Eng.* **68**, No. 19, 160 (1961).
- (11) Thilo, E., Grunze, H., *Z. Anorg. Allgem. Chem.* **281**, 262 (1955).
- (12) Van Wazer, J. R., "Phosphorus and Its Compounds," pp. 619-26, Interscience, New York, 1958.

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PHOSPHORUS AVAILABILITY

Correlations among Soil Phosphorus Fractions, Extractable Phosphorus, and Plant Content of Phosphorus

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Greenhouse and laboratory studies were conducted to determine relationships among soil phosphorus fractions, soil test methods, and millet growth and phosphorus content on three New Jersey soils, obtained from field plots previously adjusted to three levels each of phosphorus and potassium. Aluminum and iron phosphates were the predominant forms of active phosphorus in these soils. Previously applied phosphate fertilizer was found to have been fixed mostly as aluminum phosphate in the three soils. The phosphorus content of millet tops was chiefly correlated with the aluminum phosphate fraction of the three soils studied. Different soil test methods for phosphorus differed in their degree of correlation with this aluminum phosphate fraction.

ELECTRODIALYSIS is currently employed by the Soil Testing Laboratory in New Jersey for extracting soil phosphorus. In general, the phosphorus released by electro dialysis of New Jersey soils correlated with crop response (17, 18). The correlation of phosphorus and certain soils and crops has, however, been poor, and the reason for this lack of correlation needs investigation.

Three of the more active forms of phosphorus in soils are the aluminum, iron, and calcium phosphate fractions (6, 22). Some greenhouse experiments have indicated that a substantial proportion of the phosphorus required by plants can be supplied by pure iron and aluminum phosphates (31, 33), but in other experiments these phosphates have been shown to be relatively poor sources of phosphorus for plants (10, 28).

Various phosphorus extraction methods

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employed in soil testing laboratories remove and measure differing proportions of these phosphate forms (3, 7). Harper (20), Dean (17), and more recently Hanna (17) indicated that electro dialysis removed more phosphorus from calcium, magnesium, and manganese phosphates than from aluminum and iron phosphates. Cho and Caldwell (9) reported that the phosphorus extracted from soils by a 0.025*N* HCl + 0.003*N* NH₄F solution and a 0.1*N* HCl + 0.03*N* NH₄F solution as described by Bray and Kurtz (4), a 1% solution of citric acid, and a 0.5*M* sodium bicarbonate solution was highly correlated with aluminum and iron phosphates in soils. Cho and Caldwell also found that phosphorus extracted from soils by 10% sodium acetate in 3.0% acetic acid solution was well correlated with calcium phosphate. Chang and Juo (8) showed that the extent of correlation between the amounts of phosphorus extracted by several chemical methods and the total

amount of each discrete form of phosphate depends on the dominant form of soil phosphorus. Susuki, Lawton, and Doll (30) found that aluminum phosphate in soils was significantly correlated with a number of soil tests for phosphorus, while calcium phosphate and organic phosphorus were not related to any of the soil tests. Pratt and Garber (26) found that phosphorus extracted from soils by the 0.025*N* HCl + 0.03*N* NH₄F solution of Bray and Kurtz (4) was positively correlated with NH₄Cl-soluble and NH₄F-soluble phosphorus and negatively correlated with clay content.

The correlation of phosphorus extracted from soils by chemical procedures with crop yield and phosphorus content should depend in part on the relative amounts of each chemical form of phosphorus in the soil and on the relative availability of each form to extraction by the plant and by the chemical procedure used. Many factors other than chemical