

Insoluble Compounds in Ammonium Polyphosphate Made from Wet-Process Phosphoric Acid

Jumpei Ando,¹ A. William Frazier, and James R. Lehr

The insoluble materials in ammonium polyphosphates are compounds of the iron and aluminum introduced in the wet-process superphosphoric acid. The compounds were identified and characterized, and the conditions that promote their formation were determined. The amounts of insoluble mate-

rial are minimized by carrying out the ammoniation as rapidly as possible at as low a temperature as practicable and avoiding the accumulation of seeds of the insoluble compounds in the ammoniation vessel.

Ammonium polyphosphates were first produced from electric furnace superphosphoric acid (Getsinger *et al.*, 1962) and were entirely water-soluble. Use of wet-process phosphoric acid to produce ammonium polyphosphates, however, yielded products in which as much as 12% of the phosphate was citrate-insoluble (Siegel *et al.*, 1965), and some products contained significant amounts of water-insoluble citrate-soluble phases. The amount of insoluble materials was directly related to the iron and aluminum contents of the product. Satisfactory products were obtained when the iron and aluminum contents of the ammonium polyphosphates were less than 2% R_2O_3 , but products prepared from wet-process phosphoric acid usually contained more than 3% R_2O_3 .

Examinations of the insoluble phases (Frazier *et al.*, 1966) showed that the citrate-insoluble materials were members of the isomorphous series $(Fe,Al)NH_4P_2O_7$. The water-insoluble, citrate-soluble materials were mixtures of amorphous iron and aluminum orthophosphates and members of the isomorphous series $(Fe,Al)(NH_4)_3HPO_4P_2O_7$. The citrate-soluble materials can be tolerated in a solid fertilizer, but their water insolubility makes them undesirable in a liquid fertilizer, although they dissolve in a day or so in ammonium polyphosphate solutions.

In a laboratory study of the conditions that promote the formation of the insoluble compounds, the conditions of operation in the pilot plant (Slack, 1962) were simulated in sealed glass tubes equilibrated for times ranging from 10 minutes to 2 hours. Several new insoluble complex iron and aluminum phosphates were observed and were characterized by their optical properties, and their x-ray powder diffraction patterns were determined. The results indicated that the formation of the insoluble compounds could be prevented by rapid ammoniation of shallow beds

or thin films of the acid and removal of the molten product from the reaction zone as soon as the ammoniation was complete. A method of rapid ammoniation, in which the ammoniation was completed in 1 to 5 minutes, was tested in the laboratory.

SEALED-TUBE TESTS

Materials and Procedure. Mixtures with the gross chemical compositions of the ammonium polyphosphates produced in the pilot plant (Slack, 1962) from wet-process phosphoric acid were prepared from ammonium polyphosphate, superphosphoric acid (both prepared from electric furnace acid), reagent anhydrous iron and aluminum orthophosphates, mono- and diammonium orthophosphates, ammonium sulfate, and ammonium fluoride. The iron and aluminum were supplied in equimolar amounts to simulate fairly closely their proportions in wet-process phosphoric acid.

A charge of 20 grams of each raw mixture was sealed in a glass tube which was placed in a steel protection tube and heated in an oven (320° to 400° C.) to a selected temperature (monitored by a thermocouple in a well in the glass tube) in the range 220° to 260° C. in 10 to 12 minutes. The tube then was placed in a constant-temperature oven to maintain the selected temperature for the duration of the run, after which the tube was removed from the oven and the fluidity (or viscosity) of the melt was estimated by observing the rate at which it flowed in the inclined tube.

Each melt was chilled and crushed, and the pH was measured on a 10% aqueous solution of the product. The entire product was extracted with water, and the water-insoluble residue was filtered off, dried, weighed, and examined petrographically and by x-ray to identify the phases present and to determine both the amount of the citrate-insoluble $(Fe,Al)NH_4P_2O_7$ and its mole ratio $Fe_2O_3 : Al_2O_3$.

Characterization of New Compounds. Water-insoluble residues from five experimental melts were homogeneous crystal compounds in forms suitable for chemical and

Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, Ala. 35660

¹ Present address, Chuo University, Tokyo, Japan

crystallographic characterization. They comprised two new compounds and three end members of two previously characterized isomorphous series. The conditions under which the new compounds were formed are shown in Table I. The first two entries in Table I were shown chromatographically to be orthophosphates, and their empirical formulas were deduced from their chemical compositions, typical examples of which are shown in Table II. The last three entries in Table I were identified by their x-ray diffraction patterns (Frazier *et al.*, 1966).

Of the two orthophosphates, $\text{Al}_3(\text{NH}_4)_3\text{H}_2(\text{PO}_4)_4\text{F}_4$ is citrate-soluble, but $\text{Al}_2(\text{NH}_4)_3(\text{PO}_4)_3$ is not. The fluoride compound has the same x-ray diffraction pattern as "compound S," observed previously in ammoniated wet-process phosphoric acid (Ando and Akiyama, 1965).

Table I. Preparation of Insoluble Compounds in Sealed Glass Tubes

Compound	Starting Mixture, ^a Grams	Temp., ° C.	Time, Hr.
$\text{Al}_2(\text{NH}_4)_3(\text{PO}_4)_3$	APP 40, $(\text{NH}_4)_2\text{HPO}_4$ 6, AlPO_4 4	270	1.5
$\text{Al}_3(\text{NH}_4)_3\text{H}_2(\text{PO}_4)_4\text{F}_4$	APP 15, AlPO_4 3, NH_4F 3	250	1
$\text{Al}(\text{NH}_4)_3\text{HPO}_4\text{P}_2\text{O}_7$	APP 10, $(\text{NH}_4)_2\text{HPO}_4$ 5, AlPO_4 1.5	240	2
$\text{AlNH}_4\text{P}_2\text{O}_7$	APP 15, $\text{Al}_2(\text{SO}_4)_3$ 2	270	2
$\text{FeNH}_4\text{P}_2\text{O}_7$	APP 15, FePO_4 2	250	16

^a APP = ammonium polyphosphate containing 14.5% N and 59.0% P_2O_5 ; 50% of P_2O_5 was orthophosphate, 50% polyphosphate. All reagents were anhydrous.

The morphological and optical properties of the compounds in Table I are shown in Table III, and the x-ray diffraction data in Table IV.

The ratio of aluminum to iron in samples of $(\text{Fe},\text{Al})\text{-NH}_4\text{P}_2\text{O}_7$ was determined by x-ray analysis (Ando *et al.*, 1965) from the calibration curve shown in Figure 1 with sodium chloride as the internal standard. The strongest peak, at $2\theta = 15.1$ to 15.4° , was too sensitive to crystal size to be useful, and the second strongest peak, at $2\theta = 22.4$ to 22.8° , was used for the determination. Results of x-ray analyses of several of the citrate-insoluble residues agreed well with chemical analyses.

Operating Variables. The effects of composition and conditions of preparation on the solubility of the ammonium polyphosphates prepared in sealed tubes are shown in Table V, and their effects on the rate of precipitation of iron and aluminum compounds from the melts are shown in Figure 2.

In all these tests the mixtures contained 1% SO_3 , and 53 to 57% of the phosphate was present as condensed phosphates (pyrophosphates or higher). The fluidity decreased as the nitrogen, R_2O_3 , and fluorine contents were increased and the temperature was lowered; the effects of nitrogen content and temperature were the most pronounced. Melts at 260°C . that contained 13% nitrogen had about the same fluidity as melts at 220°C . that contained 12% nitrogen. Operation of the process on a pilot-plant scale is facilitated by high fluidity of the melt. High fluidity, however, permits more rapid growth of nucleating crystals, so that ease of operation under these conditions tends to increase the amount of citrate-insoluble material in the product.

Table II. Composition of Insoluble Orthophosphates

Compound	Composition, Wt. %				Moles/Mole P		
	Al	N	P	F	Al	N	F
$\text{Al}_2(\text{NH}_4)_3(\text{PO}_4)_3$ Stoichiometric	13.3	10.5	23.6	...	0.65	0.99	...
	13.73	10.69	23.64	...	0.67	1.00	...
$\text{Al}_3(\text{NH}_4)_3\text{H}_2(\text{PO}_4)_4\text{F}_4$ Stoichiometric	12.5	10.7	19.6	11.3	0.74	1.22	0.94
	12.87	11.13	19.70	12.08	0.75	1.25	1.00

Table III. Morphological and Optical Properties of Insoluble Compounds

Compound	Crystal System, Class, Habit	Refractive Indices	Optical Properties ^a
$\text{Al}_2(\text{NH}_4)_3(\text{PO}_4)_3$	Hexagonal, $6/m$. Stout rods terminated by (0001)	$N_\omega = 1.587$ $N_\epsilon = 1.586$	Uniaxial (-). $d = 2.32$
$\text{Al}_3(\text{NH}_4)_3\text{H}_2(\text{PO}_4)_4\text{F}_4$	Microscopic, length-slow needle crystals	$N_1 = 1.529$ $N_2 = 1.536$	
$\text{Al}(\text{NH}_4)_3\text{HPO}_4\text{P}_2\text{O}_7$	Orthorhombic, mmm . Blade crystals tabular on Y-Z plane	$N_\alpha = 1.535$ $N_\beta = 1.543$ $N_\gamma = 1.559$	Biaxial (+). $2V = 72^\circ$ calcd. OAP \perp tabular plane. $d = 2.07$
$\text{AlNH}_4\text{P}_2\text{O}_7$	Microscopic prismatic crystals too small for classification	$N_{\text{mean}} = 1.586$	$d = 2.57$
$\text{FeNH}_4\text{P}_2\text{O}_7$	Monoclinic, $2/m$. Rod crystals elongated along a or c	$N_\alpha = 1.680$ $N_\beta = 1.695$ $N_\gamma = 1.705$	Biaxial (-), $2V = 78^\circ$ calcd. OAP = (010), $Y = b$. $d = 2.71$

^a All values for densities calculated by Gladstone-Dale equation (Larsen and Berman, 1943).

Table IV. X-Ray Powder Diffraction Data^a

Al ₂ (NH ₄) ₃ - (PO ₄) ₃		Al ₃ - (NH ₄) ₃ H ₂ - (PO ₄) ₄ F ₄		Al(NH ₄) ₃ - HPO ₄ - P ₂ O ₇		AlNH ₄ - P ₂ O ₇		FeNH ₄ - P ₂ O ₇	
2θ	I	2θ	I	2θ	I	2θ	I	2θ	I
11.2	9	7.9	40	11.3	93	15.4	79	15.1	100
17.3	100	8.5	15	12.1	44	16.9	12	16.6	28
20.3	8	10.2	8	13.5	100	18.4	15	17.7	16
26.6	6	11.7	10	17.3	35	21.2	17	20.9	8
27.2	15	14.6	10	17.5	27	21.6	36	22.4	78
28.0	7	14.8	80	19.3	20	22.8	73	25.9	14
29.0	16	15.8	100	20.2	5	26.6	12	26.9	10
30.1	66	16.8	65	20.4	5	28.7	14	28.7	14
31.8	4	21.6	5	20.7	6	29.4	13	29.5	52
35.0	35	22.8	10	21.8	12	30.5	100	29.8	50
36.5	4	24.2	7	22.2	3	34.5	7	30.0	58
37.1	5	28.2	20	22.7	24	36.1	5	33.8	14
46.8	6	30.0	45	23.6	4	37.3	12	35.5	6
51.5	4	30.4	60	24.6	4	37.6	7	35.9	11
53.5	15	30.9	85	25.8	51	38.9	9	36.9	20
		31.9	20	26.5	14	39.4	7	44.0	10
		33.0	10	27.4	23	42.1	5	45.5	12
		33.6	7	28.8	6	43.8	4	51.9	10
		34.2	10	29.4	12	46.6	11	53.2	9
		35.2	10	30.0	38	49.5	5	58.4	12
		39.1	7	30.4	32	52.8	9	59.0	10
		40.3	4	30.8	7	53.9	4		
		40.9	5	31.3	9	54.8	6		
		42.9	5	32.2	8	57.3	5		
		43.2	4	32.8	7	57.7	5		
		46.5	4	33.6	4				
		48.8	13	34.5	31				
		49.5	5	34.8	22				
		51.4	5	35.6	6				
		53.1	16	36.3	4				
		56.1	5	39.0	14				
				40.2	10				
				41.3	4				
				42.1	4				
				44.6	6				
				46.4	5				
				47.4	9				
				50.4	7				

^aData obtained with x-ray diffractometer, CuK_α radiation, λ = 1.5405 Å. Intensities measured as peak heights above background, and expressed as per cent of strongest line.

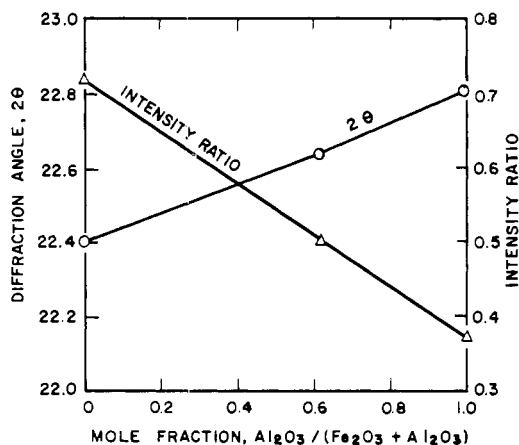


Figure 1. Calibration curve for (Fe,Al)NH₄P₂O₇

Intensity ratio is ratio of height of peak of sample to that of 31.8° 2θ peak of NaCl when weight ratio (Fe,Al)NH₄P₂O₇ : NaCl = 4.

The interactions among the several variables of the operating conditions are shown in Table V. The citrate-insoluble material was formed more rapidly at a higher temperature and a lower nitrogen content of the melt—and hence a higher fluidity—than at a lower temperature and higher nitrogen content. Thus, in the melt containing 12% nitrogen, nearly all the R₂O₃ was precipitated as citrate-insoluble material in 120 minutes at 220° C. but in only 10 minutes at 260° C. The rate of precipitation of R₂O₃ was about as high in a melt at 240° C. that contained 12% nitrogen as in a melt at 260° C. that contained 13% nitrogen, and these melts had about the same high fluidity. A melt that contained 13% nitrogen had medium fluidity at 220° C., and a melt that contained 15% nitrogen had low fluidity at 260° C.; very little citrate-insoluble material was formed under either of these conditions.

Fluorine, which complexes iron and aluminum, decreased the rate of formation of the citrate-insoluble material. The complex of fluorine with aluminum is stronger than that with iron, and the mole ratio Fe:Al in the citrate-insoluble compound was almost always 1 or more and tended to increase with increase in the fluorine content.

On the other hand, fluorine increased the amount of water-insoluble, citrate-soluble amorphous material. When the fluorine content was increased from 0.5 to 2%, large amounts of the amorphous material formed rapidly in the melts and then altered slowly to the citrate-insoluble compound as long as the mixture remained molten. In two melts that contained 2% fluorine, considerable amounts of Al₃(NH₄)₃H₂(PO₄)₄F₄ were formed. The iron analog of this compound has not been observed, but iron probably can substitute for some of the aluminum.

In four melts (14, 18, 22, 26) that contained only 2% R₂O₃ and were heated for 120 minutes, about the same fraction of the R₂O₃ was precipitated as citrate-insoluble material as in corresponding melts (17, 21, 25, 27) that contained 5% R₂O₃ and had otherwise the same composition and were heated for the same length of time at the same temperature. These results confirm the earlier observation (Siegel *et al.*, 1965) that the amount of citrate-insoluble material is proportional to the R₂O₃ content.

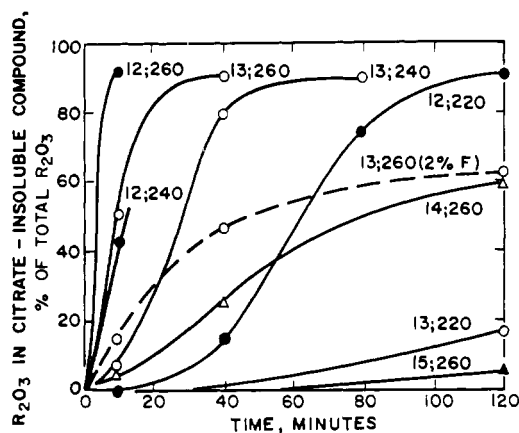


Figure 2. Formation of citrate-insoluble material in ammonium polyphosphates prepared in sealed tubes

Melts contained 5% R₂O₃, 0.5% F. Numbers on curves denote N content, %, and temperature, °C.

Table V. Ammonium Polyphosphates Prepared in Sealed Tubes
(1% SO₃; 53-57% of P₂O₅ present as polyphosphate)

No.	Composition, Weight %				Conditions of Prepn.		Fluidity of Melt ^a	pH ^b	Fraction, % of Product ^c		Atomic Ratio Fe:Al in CI Material	Fraction, % of R ₂ O ₃ Pptd. as CI	Water-Insol., Cit.-Soluble Phase ^d
	N	R ₂ O ₃	F	P ₂ O ₅	Temp., ° C.	Time, min.			WI	CI			
1	12	5	0.5	62	220	10	High	3.2	1.0	0	...	0	A
2	12	5	0.5	62	220	40	High	3.5	7.9	3	1.5	17	A
3	12	5	0.5	62	220	80	High	3.6	15.3	13	1.0	74	A
4	12	5	0.5	62	220	120	High	3.6	17.1	16	1.0	91	A
5	12	5	0.5	62	240	10	High	3.6	9.1	8	1.0	45	A
6	12	5	0.5	62	260	10	High	3.6	16.9	16	1.0	91	A
7	13	5	0.5	61	220	10	Med.	4.4	2.2	0	A
8	13	5	0.5	61	220	120	Med.	4.5	7.7	3	1.0	17	A
9	13	5	2	60	220	10	Med.—	4.2	12.3	0.1	...	1	A, B
10	13	5	2	60	220	120	Med.—	4.3	15.7	0.3	...	2	A, B
11	13	5	0.5	61	240	10	High	4.4	3.8	1	1.5	6	A
12	13	5	0.5	61	240	40	High	4.8	14.3	14	1.0	80	A
13	13	5	0.5	61	240	80	High	4.8	16.5	16	1.0	91	A
14	13	2	0.5	63	260	120	High	4.4	7.0	6	1.0	84	A
15	13	5	0.5	61	260	10	High	4.6	10.6	9	1.0	51	A
16	13	5	0.5	61	260	40	High	4.8	16.3	16	1.0	91	A
17	13	5	0.5	61	260	120	High	4.8	16.2	16	1.0	91	A
18	13	2	2	61	260	120	High	4.2	5.6	4	2.5	60	A
19	13	5	2	60	260	10	Med.	4.3	14.9	3	9.0	19	A
20	13	5	2	60	260	40	Med.+	4.4	15.7	8	1.5	47	A
21	13	5	2	60	260	120	Med.+	4.5	16.7	11	1.5	63	A
22	14	2	0.5	61	260	120	Med.+	4.9	6.1	4	1.0	56	A
23	14	5	0.5	60	260	10	Med.	5.0	12.9	2	1.0	11	D
24	14	5	0.5	60	260	40	Med.	5.1	14.5	6	1.0	34	D
25	14	5	0.5	60	260	120	Med.	5.2	16.7	11	1.0	63	D
26	14	2	2	60	260	120	Med.	4.6	4.7	3	2.5	45	A
27	14	5	2	59	260	120	Low	5.0	15.9	7	2.5	42	D
28	15	5	0.5	59	260	10	Low	6.0	15.3	0	...	0	D
29	15	5	0.5	59	260	120	Low	6.0	18.0	1	0.5	5	D

^a At high fluidity, melt flowed easily in sealed glass tube; at low fluidity, melt was too viscous to flow appreciably before it solidified. Med. = medium.

^b Measured on 10% aqueous solution.

^c Water- (WI) and citrate-insoluble (CI) fractions determined by official methods (Assoc. Offic. Agr. Chemists, 1965). WI includes CI.

^d A = amorphous material, B = Al₃(NH₄)₃H₂(PO₄)₄F₄, D = (Fe,Al)(NH₄)₃HPO₄P₂O₇.

In products with pH (determined on 10% aqueous solution) below 5, the water-insoluble, citrate-soluble material was amorphous; it contained 45 to 51% P₂O₅ and some fluorine. In products with pH above 5, this fraction consisted of crystalline (Fe,Al)(NH₄)₃HPO₄P₂O₇. Precipitation of this compound in the early part of a test decreased the R₂O₃ content of the melt with a resultant decrease in the formation of the citrate-insoluble (Fe,Al)-NH₄P₂O₇. In other runs (not reported in Table V) in which the melt contained 4% Al₂O₃ and no iron, the new compound Al₃(NH₄)₃(PO₄)₃ was formed along with AlNH₄-P₂O₇ and Al(NH₄)₃HPO₄P₂O₇. This new compound was never observed in melts containing iron.

In a few runs (not reported in Table V), the SO₃ content of the melt was increased to 5%. The increased sulfate content raised the fluidity of the melt with resultant increase in the formation of insoluble compounds, but this effect was not highly significant.

Polyphosphate Content. In the runs reported in Table V, the polyphosphate content of the melts ranged only from 53 to 57% of the total P₂O₅, but in plant operation the polyphosphate content may range from 30 to 70%. In tests of the effect of the polyphosphate content, runs

were made with mixtures containing 5% R₂O₃, 1% SO₃, and 0.5% F; the polyphosphate content was varied from 30 to 70%. Two levels of nitrogen content, 13 and 14% N, were used, and the melts were held at 240° C. for 40 minutes (Table VI).

In the mixtures containing 13% nitrogen, increase in the polyphosphate content from 31 to 69% of the total P₂O₅ increased the fluidity, decreased the amount of water-insoluble, citrate-soluble material, and increased the amount of citrate-insoluble material. The decrease in the amount of water-insoluble, citrate-soluble material is attributed to the higher sequestering capacity of the larger amount of polyphosphate, but this sequestering capacity did not prevent the formation of citrate-insoluble material.

No citrate-insoluble material was formed in the two mixtures that contained 14% nitrogen, but the increase in polyphosphate content from 56 to 71% decreased considerably the amount of water-insoluble, citrate-soluble material, all of which was present as crystalline (Fe,Al)(NH₄)₃HPO₄P₂O₇. The cooled melts of these two mixtures had very poor physical properties; they were sticky and crystallized very slowly.

Table VI. Effect of Polyphosphate Content on Formation of Insoluble Compounds

(Melts held at 240° C. for 40 minutes)

N Content, %	Polyphosphate P ₂ O ₅ , % of Total	Water-Insoluble ^a Precipitate, % of Total Weight	
		Citrate- soluble	Citrate- insoluble
13	31	11	6
	42	6	10
	57	1	14
	69	1	13
14	56	11	0
	71	7	0

^a Determined by official methods (Assoc. Offic. Agr. Chemists, 1965).

Effect of Seeds. As shown in Table V and Figure 2, nucleation of the citrate-insoluble (Fe,Al)NH₄P₂O₇ is slow. In continuous ammoniation in a pilot plant, however, crystals of this material are always present to accelerate the precipitation of the insoluble compound. In a study of the effect of seeds on the rate of formation of the insoluble compound, mixtures were prepared that contained 12% nitrogen, 5% R₂O₃, 62% P₂O₅ (55% of the P₂O₅ was present as polyphosphate), and 0.5% fluorine, and to half of the mixtures was added 1% of a water-insoluble material that had been separated from the product of a previous run. This insoluble material contained both amorphous material and crystals of (Fe,Al)NH₄P₂O₇ smaller than 1 micron. The mixtures were heated at 220° C. for 10 to 120 minutes (Table VII).

The seeds accelerated the formation of both types of insoluble compounds, and this effect was more pronounced with the citrate-insoluble material than with the water-insoluble, citrate-soluble material. Seeding also increased the size of the crystals of (Fe,Al)NH₄P₂O₇. The seeds were smaller than 1 micron, but the crystals of this material in the seeded melts were larger than 1 micron, whereas those in the unseeded melts were smaller than 1 micron. In pilot-plant products, the crystals of (Fe,Al)NH₄P₂O₇ grow as large as 3 microns.

RAPID-AMMONIATION TESTS

As long retention in the ammoniation vessel, particularly in the presence of seeds, promoted formation of the citrate-insoluble (Fe,Al)NH₄P₂O₇, it appeared desirable to carry out the ammoniation in as short a time as possible. In a study of this modification, shallow pools of acid were ammoniated rapidly, and the cooled melts were examined as before. The acid contained 54.9% P₂O₅, 2.1% Fe₂O₃, 1.3% Al₂O₃, 0.4% CaO, 0.05% K₂O, 0.9% SO₃, and 0.5% F. The mole ratio R₂O₃:P₂O₅ in the acid was 0.067, in the upper range of R₂O₃ content of clarified wet-process acid.

A charge of 10 grams of the acid was placed in a flat-bottomed platinum dish to form a pool about 4 mm. deep, and the dish was placed on a hot plate that was heated to 200° to 240° C. When the temperature of the acid rose to a selected value in the range 120° to 175° C., the acid

Table VII. Effect of Seeding on Formation of Insoluble Material

(Melts containing 12% N held at 220° C.)

Time, Min.	Water-Insoluble Precipitate, % of Total Weight ^a			
	Without Seeding		Seeded Melts	
	Citrate- soluble	Citrate- insoluble	Citrate- soluble	Citrate- insoluble
10	1.0	0.0	3.0	1.5
40	4.5	3.0	5.5	8.0
80	2.5	13.0	0.5	16.0
120	1.0	16.0

^a Solubilities determined by official methods (Assoc. Offic. Agr. Chemists, 1965).

was treated for 50 to 600 seconds with 3.4 grams of ammonia per minute, introduced through a glass tube which was used also to stir the melt.

At about 190° C. evaporation of water caused marked frothing which increased the depth of the acid to about 30 mm. The frothing subsided in 30 to 40 seconds, leaving a viscous melt of ammonium polyphosphate. Maximum temperature was attained in 50 to 100 seconds of ammoniation, depending on the initial temperature of the acid, and the temperature then remained fairly constant when ammoniation was continued for a total of 200 seconds. On further ammoniation, the temperature dropped 5° or 10° C. below the maximum. When ammoniation was discontinued, the platinum dish was removed from the hot plate and allowed to cool rapidly to room temperature in an atmosphere of ammonia. Most products solidified at about 180° C. to form a layer 3 mm. thick.

As shown in Table VIII, melts containing as little as 11.2% N and almost no insoluble materials were prepared by rapid thin-film ammoniation at 235° C. This contrasts sharply with the results obtained in sealed tubes (Table V and Figure 2), where conditions simulated those in the relatively slow ammoniation of deep pools. In the tube experiments, formation of insoluble material was accelerated as the ammonia content of the melt was lowered with resultant increase in acidity and fluidity; when the melt contained 12% N, formation of insoluble material was rapid at temperatures above 220° C.

The loss of water in the rapid-ammoniation tests increased both the P₂O₅ content of the product and the fraction of the P₂O₅ converted to polyphosphates, and there was a practically linear relation between the P₂O₅ content and the fraction of the P₂O₅ present as polyphosphate. In contrast to the results of the sealed-tube tests in Table VI, the effect of the polyphosphate content of the rapid-ammoniation products on the formation of insoluble material was not significant at polyphosphate contents below about 65%. When the polyphosphate content rose above 65%, the citrate-insoluble content increased considerably, particularly at higher temperatures.

The data in Table VIII show that, under an ammonia pressure of 1 atm., temperature and time of heating are the major factors that determine the solubility of the am-

Table VIII. Ammonium Polyphosphate Prepared by Rapid Ammoniation

Test	Reaction Conditions				Product							
	Preheating		Ammoniation		Compn.		P ₂ O ₅ , % of Total ^a				pH ^b	DOA ^c
	Time, sec.	Max. temp., ° C.	Time, sec.	Max. temp., ° C.	N	P ₂ O ₅	Poly.	WS	DA			
31	0	25	120	240	12.6	60.1	54.0	97.0	99.4	4.8	5.1	
32	50	120	60	235	12.0	60.8	52.3	98.2	100.0	4.3	4.8	
33	50	120	100	235	12.4	60.9	57.8	98.9	100.0	4.6	5.0	
34	50	120	200	235	12.5	61.3	62.2	98.3	99.2	4.7	5.0	
35	50	120	60	250	11.5	61.6	60.3	98.1	99.7	3.9	4.5	
36	50	120	100	250	11.9	62.3	69.5	98.0	99.2	4.0	4.6	
37	50	120	200	250	12.2	62.8	76.2	97.0	97.2	4.0	4.7	
38	60	135	100	235	12.3	60.8	57.0	99.0	100.0	4.5	4.9	
39	60	140	120	265	11.8	63.3	73.6	97.7	98.2	3.9	4.5	
40	75	150	60	235	12.0	61.4	59.7	99.0	100.0	4.2	4.8	
41	75	150	100	235	11.9	61.8	61.8	99.2	100.0	4.3	4.7	
42	90	165	50	235	11.2	62.8	64.2	99.7	100.0	3.8	4.4	
43	90	165	100	235	11.6	62.8	66.4	99.5	99.8	4.0	4.5	
44	90	165	300	235	12.2	62.3	68.9	96.5	97.5	4.6	4.8	

Effects of Long Retention Time and High Temperature

45	90	165	600	235	12.6	62.9	72.5	91.8	93.5	4.6	4.8
46	90	165	300	250	12.4	63.3	81.5	93.7	95.3	4.3	4.7
47	90	175	100	280	11.5	64.4	79.4	93.8	94.0	3.6	4.4
48	90	175	180	280	11.8	64.8	88.3	88.0	88.2	3.8	4.4

^a WS = water-soluble, DA = direct available, determined with neutral ammonium citrate solution (Assoc. Offic. Agr. Chemists, 1965).

^b Measured on 10% aqueous solution of product.

^c Degree of ammoniation, pounds NH₃/unit P₂O₅.

monium polyphosphate products. The combined effects of temperature and time of ammoniation are shown in Figure 3. In the ranges studied, the effects of the preheating time and temperature were slight compared with those of the ammoniation time and temperature. The curves in Figure 3 show that ammonium polyphosphates with 97% or more of their P₂O₅ available are obtained with maximum ammoniation times of 1 minute at 280° C., 2 minutes at 265° C., 3 minutes at 250° C., or 5 minutes at 235° C.

DISCUSSION

The most important factor in the formation of insoluble material is the iron and aluminum content of the wet-process phosphoric acid from which the ammonium polyphosphate is prepared. The temperature and time of ammoniation are the most important operating variables. The nitrogen content of the melt also has considerable effect on the rate of formation of insoluble material, and useful correlation of the results of both the sealed-tube and rapid ammoniation tests may be made through use of the ratio T/N , where T is temperature, ° C., and N is nitrogen content, %, of the melt. Results of both types of tests are summarized in Figure 4 for products containing about 0.5% F, 1% SO₃, 3.7 to 5% R₂O₃, 11 to 13% N, and 60 to 63% P₂O₅, more than 53% in the form of polyphosphate.

As shown in Figure 4, the rate of formation of citrate-insoluble material increases as the ratio T/N increases. These data are further summarized in Figure 5 to define the conditions required for products in which 97% or more of the P₂O₅ is citrate-soluble—for example, if a product containing 12% nitrogen is to be prepared at 250° C.

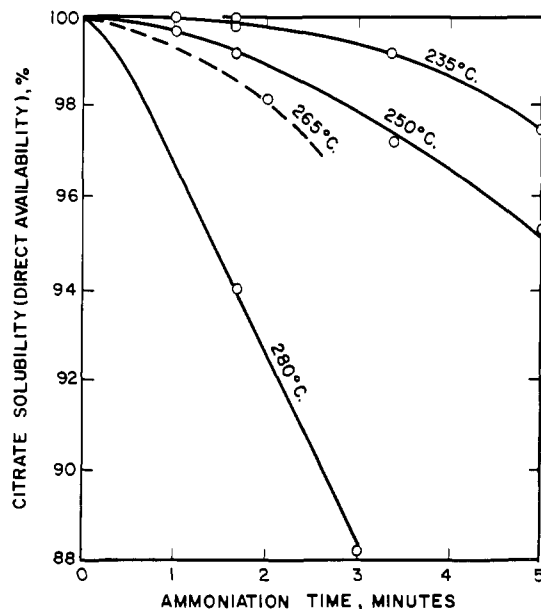


Figure 3. Effect of ammoniation time and temperature on availability of ammonium polyphosphates prepared by rapid ammoniation

($T/N = 20.7$), the reaction time must be no longer than 2.5 minutes if the R₂O₃ content is 5% or 4 minutes if the R₂O₃ content is 3% to maintain a citrate solubility of the P₂O₅ of at least 97%.

Increasing the nitrogen content above 14% increases the formation of citrate-soluble (Fe,Al)(NH₄)₃HPO₄P₂O₇ and decreases the formation of citrate-insoluble material, so

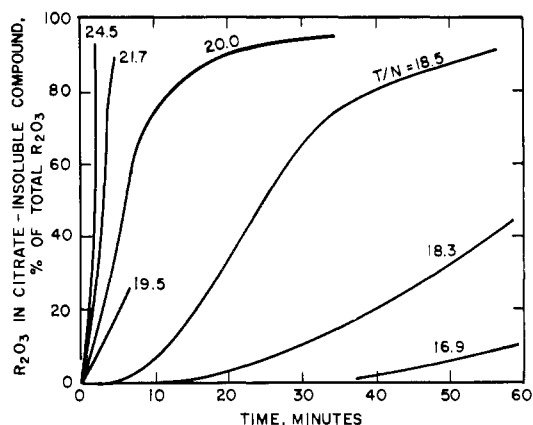


Figure 4. Rate of formation of citrate-insoluble material in ammonium polyphosphates

that at high nitrogen contents somewhat longer times than indicated in Figure 5 may be tolerated. Decreasing the polyphosphate content below 50% of the total P_2O_5 also lengthens the permissible reaction time somewhat.

On the other hand, the presence of seeds in the initial acid shortens the permissible reaction time. In a reactor in which the acid and ammonia are introduced into a pool of ammoniated melt, seeds of the insoluble compounds are always present to accelerate the formation of insoluble material. Rapid ammoniation is difficult to obtain in a deep pool of a relatively viscous melt, and other types of reactors, in which relatively thin layers of melt are ammoniated rapidly, should yield products containing minimum amounts of insoluble compounds. In a pilot-plant study of the process (Davis and Lee, 1967), means were developed for producing an ammonium polyphosphate with high phosphate availability.

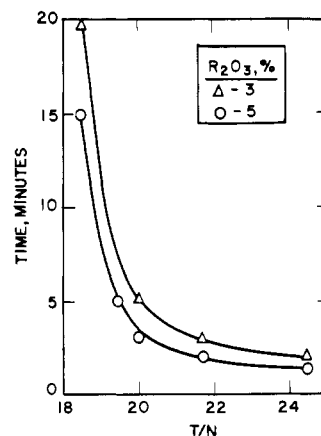


Figure 5. Conditions required for maintenance of high citrate solubility of ammonium polyphosphates

Materials prepared under conditions below and to left of curves are at least 97% citrate-soluble

T = temperature, °C. N = nitrogen content, %

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