ammonium polyphosphate in amounts equal to 20 to 30% of the P_2O_5 in the solution effectively sequestered the impurities which would have precipitated from the acid. The solutions (8–24–0 and 6–18–6) were free of solids.

Discussion

Bench-scale production of ammonium polyphosphate yielded a granular product requiring no drying and having a plant-food content of 77 to 78%, which is higher than in any combination fertilizer known at present.

The use of moderate pressure for the reactor eliminates the need for a scrubber to recover ammonia. Further studies are being carried out in pilot-plant scale equipment where the ammonia feed system was made automatic by use of a pressure regulating valve in the feed line. The temperature and level control could be made automatic also, giving completely automatic control of the reactor.

Use of Wet-Process Phosphoric Acid

Exploratory studies have been started on the production of ammonium polyphosphates from highly concentrated wet-process phosphoric acid (about 72% P_2O_5) and ammonia. The production of this acid from merchant-grade acids

is described by Scott (4). In general, the ammonium polyphosphates were produced from the highly concentrated phosphoric acid by the same operating procedure used in tests with superphosphoric acid.

Only one acid, produced from Florida rock, has been tested thus far. It had the following analysis:

Acid analysis, % by weight					
Total P_2O_5	Ortho P_2O_5	F	SO_3	Al_2O_3	Fe_2O_3
71.7	36.2	0.3	2.5	1.3	1.6

In the first tests, an unsatisfactory product was obtained at 25 p.s.i.g. and 375° F. The degree of ammoniation was only about 6.2 pounds of ammonia per unit of total P_2O_5; the product was very hygroscopic and caked severely in accelerated caking tests. A hard, less hygroscopic product was obtained when the pressure was increased to 300 p.s.i.g. and the temperature was 425° F. At this reactor pressure, 6.5 pounds of ammonia per unit of total P_2O_5 were fixed and the product had a grade of 15–58–0. The degree of ammoniation and product grade were less than obtained under the best operating conditions with superphosphoric acid (7.4 lb. NH_3 per unit of P_2O_5 and a grade of 18–59–0).

Studies of the production of ammonium polyphosphate from highly concentrated wet-process acids are being continued.

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FERTILIZER MATERIALS

Melting Points in Orthophosphoric Acid–Pyrophosphoric Acid System

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FERTILIZER TECHNOLOGISTS recently saw the introduction of superphosphoric acid (17, 18) as a material equivalent to about 105% orthophosphoric acid in the manufacture of solid (13) and liquid (19) fertilizers. Its phosphoric oxide content (about 76%) places superphosphoric intermediate in composition between orthophosphoric acid (72.4% P_2O_5) and pyrophosphoric acid (79.8% P_2O_5). Occasions for its storage and shipment in winter lead to interest in the freezing points of compositions in the ortho-pyro range.

The early work with superphosphoric acid as a fertilizer material demonstrated qualitatively its outstanding characteristics of fluidity, including its persistence as a liquid when strongly supercooled over long periods, even when seeded. Although advantageous in a practical way, these characteristics introduced formidable difficulties in the measure-

ments presented here as a basis for a melting-point diagram of the orthophosphoric-pyrophosphoric region of the system phosphoric oxide–water.

Methods

Solid phosphoric oxide was dissolved in orthophosphoric acid (reagent grade) to yield a stock solution which was filtered, then stirred 2 hours at 135° C. to promote equilibrium among the species of phosphoric acid. This solution (81% phosphoric oxide) was diluted to make secondary stock solutions of integral concentrations which were blended to yield specific gross concentrations for the measurements.

Ten-milliliter charges of the various acid compositions, seeded with ortho or pyro crystals as appropriate, were sealed in 12-mm. borosilicate glass tubes and

stored at room temperature or at 7° C. until crystallization was essentially complete. In the absence of seed, compositions with melting points below room temperature were difficult to crystallize; rapid cooling by immersion in solid carbon dioxide or liquid nitrogen produced glasses instead of crystals.

The tubes of crystals were mounted on a rocker in a water bath and oscillated through an arc of 110°—enough to wet the walls with liquid phase as the crystals melted. By means of an electronic controller, the temperature was raised in steps of 1° or 2° C. until liquid phase appeared, then at a rate of 0.1° C. per day until the proportion of solid phase was 5% or less, and finally at a rate of 0.05° C. per day to disappearance of crystals, and the temperature then was taken as the melting point. Temperatures were read on a Beckmann thermometer that was checked against a

A melting-point diagram is presented for the orthophosphoric acid–pyrophosphoric acid region of the phosphoric oxide–water system—a region embracing the superphosphoric acid compositions (about 76% phosphoric oxide) recently introduced in the manufacture of solid and liquid fertilizers. The diagram was derived through a slow-melting technique necessitated by a marked tendency toward supercooling. A eutectic occurs at 75.4% phosphoric oxide and 16.0° C. At higher contents of phosphoric oxide, pyrophosphoric acid crystallizes in two forms—the usual (metastable; m.p., 54.3° C.) and a new one (m.p., 71.5° C.) for which x-ray diffraction data are given. The diagram has immediate practical value in the storage and handling of superphosphoric acid.
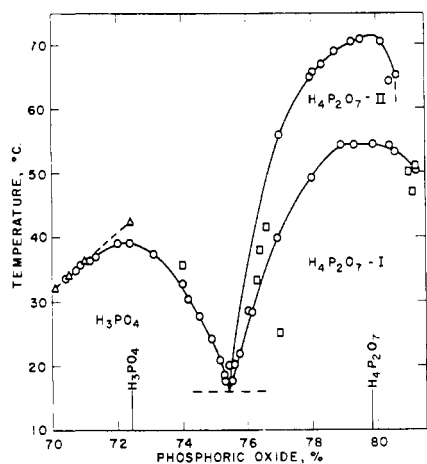

Figure 1. Melting-point diagram for orthophosphoric acid–pyrophosphoric acid system

△ Ross and Jones (14)
□ Bassett (2)
○ This work

Table I. Melting Points in Orthophosphoric Acid–Pyrophosphoric Acid System

Solid Phase, H₃PO₄		Solid Phase, H₄P₂O₇-I		Solid Phase, H₄P₂O₇-II	
P_2O_5, %	M.p., ° C.	P_2O_5, %	M.p., ° C.	P_2O_5, %	M.p., ° C
70.43	33.63	75.48	19.67	76.96	55.51
70.74	34.80	75.5[a]	17.71	77.95	64.80
70.80	35.86	75.50	17.67	78.02	65.51
70.91	35.75	75.56	20.17	78.30	66.78
71.11	36.30	75.59	20.10	78.70	68.83
71.15	36.00	75.76	21.82	79.29	70.38
71.18	37.03	75.78	21.82	79.50	70.74
71.33	36.97	75.97	28.51	80.13	70.38
71.98	38.85	76.14	28.34	80.4[a]	64.20
72.40	38.85	76.93	39.80	80.6[a]	65.07
73.06	37.45	77.97	49.06		
73.15	37.31	78.89	54.21		
73.80	32.37	79.3[a]	54.30		
73.97	32.56	79.5[a]	54.30		
74.16	30.45	79.9[a]	54.30		
74.17	30.45	80.35	54.07		
74.51	27.58	80.55	53.09		
74.90	24.10	81.2[a]	50.26		
75.15	20.83				
75.26	18.57				
75.32	17.57				

[a] Composition by weight dilution.

platinum resistance thermometer at least once in each setting range.

On completion of a measurement, the phosphoric oxide content of the charge was determined by the differential spectrophotometric method of Gee and Deitz (5).

Because of the supercooling phenomenon, a melting-point cell (7) gave satisfactory measurements only for near-ortho compositions. The measurements reported here were obtained with the rocking device.

Their x-ray patterns served for differentiation between the solid phases. For x-ray examination, an acid composition was adjusted in temperature to form a slurry of crystals, which was sucked into a special x-ray capillary. The ends were sealed with low-melting Apiezon wax, and the tubes were stored at 7° C. until over half the acid was crystalline.

Observations

The system is far from ideal; it con-tains several species of phosphoric acid in addition to the principal ones—ortho and pyro (3, 9, 11, 12). The observed melting points are related here to gross compositions, however, without attempt to correlate them with relative proportions of the various species.

The observed melting points are listed in Table I and are plotted in Figure 1. Points are included in Figure 1 from Ross and Jones (14) for near-ortho compositions and from Bassett (2) for scattered compositions. Bassett's point at 77.06% phosphoric oxide and 25° C. appears to be in error.

The melting-point diagram shows a eutectic at 75.4% phosphoric oxide and 16.0° C.—the lowest temperature at which liquid phase appeared. A eutectic at 76% and 15° C. was reported by Van Wazer (20) from unpublished data. Compositions richer in phosphoric oxide show solid phases of two crystalline forms of pyrophosphoric acid, designated as I and II. Evidence of the existence of two crystalline forms of pyrophosphoric acid was noted several years ago by Hill (10).

The melting curve for pyrophosphoric acid-I (the common form) rises smoothly to a flat portion at 54.3° C. extending from 79.29 to 79.88% phosphoric oxide. This maximum is taken as the transition temperature of I → II. Solid-solid

transition was not observed. When slurries containing pyrophosphoric acid-I were heated over the range 50° to 54° C. without stirring, the solid melted until only a few crystals remained. With further increase in temperature, the solid content increased until (at about 60° C.) the entire mass was solid. Once formed in this manner, pyrophosphoric acid-II remained stable at room temperature and could be used to seed other charges.

A melting point of 71.5° C. for pyrophosphoric acid-II was obtained by extrapolation from a plot of log mole fraction against reciprocal temperature (° K.) for three experimental points (Table I) approaching the theoretical phosphoric oxide content (79.76%) from the low side. A melting point of 61° C. for pyrophosphoric acid was reported by Giran (6) in 1902, but he was not clear about the composition.

The x-ray powder diffraction pattern of pyrophosphoric acid-II, represented by the interplanar spacings and estimated intensities in Table II, is distinctly different from the pattern of pyrophosphoric acid-I (1). Powder diffraction data for orthophosphoric acid are not

Table II. X-Ray Powder Diffraction Data for Pyrophosphoric Acid-II^a

d	I	d	I	d	I
5.20	M	2.54	MS	1.77	W
4.62	S	2.33	W	1.75	W
4.45	M	2.21	W	1.62	WM
4.30	VS	2.15	W	1.59	WM
3.69	S	2.10	W	1.57	WM
3.39	M	1.99	W	1.55	WM
3.18	VS	1.97	W	1.49	WM
3.11	VS	1.91	WM	1.48	M
2.67	MS	1.88	WM	1.44	WM
2.59	MS				

^{a} Measurements made by James P. Smith. Camera diameter, 14.32 cm.; CuKα radiation. Intensities estimated visually: VS, very strong; S, strong; MS, medium strong; M, medium; WM, weak medium; W, weak.

available, but the interplanar spacings may be calculated from structural data reported by Smith, Brown, and Lehr (16).

In approaches to the melting point of orthophosphoric acid from the direction of a deficiency of phosphoric oxide, Ross and Jones (14) concluded that the melting point is 42.35° C., whereas Smith and Menzies (15) reported 42.32° C. A lower value is indicated by present measurements from both directions of concentration. Melting points by the slow melting technique agreed (Figure 1) with the data of Ross and Jones in the range 70.6 to 71.0% of phosphoric oxide, then curved to a maximum of 38.85° C. for the composition corresponding to orthophosphoric acid.

The melting behavior is illustrated by the results obtained with three presumably identical charges, A, B, and C, containing 72.4% phosphoric oxide. On the first heating, A and B melted at 41.0° C., whereas C still contained 30% of crystals. Successive slow-melting tests of sample B alone gave melting points of 39.56°, 39.25°, and 38.74° C. Samples A and C were tested in short-time freezing and melting cycles with an arbitrary refreezing temperature of 36° C. When the temperature was raised to 39.56°, 39.25°, 39.13°, and 38.92° C. in successive tests, A melted in 1 or 2 hours at each temperature, whereas C remained essentially unchanged at 1% liquid phase under the same conditions. When the temperature was raised slowly over a 10-day period, A, B, and C all melted

at 38.85° C., although the time to the disappearance of crystals varied by 1 or 2 days.

There is evidence (4) that orthophosphoric acid begins a rearrangement with formation of pyrophosphoric acid and water when melted. The behavior on melting of orthophosphoric acid suggests that melting of the crystals in immediate contact with essentially pure liquid orthophosphoric acid may yield melting-point values approximating that reported by Ross and Jones (14), whereas slow melting of the crystals in contact with liquid phase that has had time to approach the equilibrium content of other species of phosphoric acid leads to the lower value found here. Between these extremes, observed melting points presumably will be related to the thermal history of the acid. This observation is supported by Greenwood and Thompson (8) who found that the first melting point of orthophosphoric acid was 40° C., but that when the liquid phase was repeatedly decanted off, the final melting point was 42.35° C.

When a charge having near-pyro composition and containing crystals of pyro-I was carried through a melting procedure in the relatively short time of 7 hours, the observed melting point was 1° C. above the established maximum for pyro-I.

Another possible factor in the melting phenomena is the formation of a solid solution of ortho or pyro with some other species of phosphoric acid (3, 9, 11, 12). The extent of formation of solid solution would be influenced by kinetic factors as well as by thermodynamic equilibrium during crystal growth. Noteworthy is the divergent behavior of three presumably identical charges (75% phosphoric oxide) simultaneously seeded from the same batch of ortho crystals and stored at 7° C. One practically solidified in 1 day and one in 4 days, whereas the third contained only 10% of crystals after 15 days.

The results reported here, although lacking in refinement, are of practical value to manufacturers of phosphoric acids. They show that superphosphoric acid that is least likely to crystallize during storage in cold weather or for long periods should have a composition in the narrow range 75 to 76% phosphoric oxide. The melting points were determined with acids prepared from reagent-

grade chemicals, but the results were shown to be applicable to commercial-grade acid. Three samples of super-phosphoric acid from the Tennessee Valley Authority demonstration plant all showed melting points that agreed with Figure 1 within the limits of error in routine analysis for phosphoric oxide when each sample was seeded and stored at 7° C. until crystallization occurred.

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